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Contents

Distribution of Petroleum in the U.K.—The Changing Pattern
By T. W. Mathias

Acid Treatment of Shale Gasoline
By Geo. E. Mapstone *et al*

Special General Meeting

Obituary—Prof. J. S. S. Brame, C.B.E.

Abstracts Book Reviews Additions to Library

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THE INSTITUTE OF PETROLEUM

An Ordinary General Meeting of the Institute was held at 26 Portland Place, London, W.1, on 22 October 1952, the President, H. S. Gibson, C.B.E., in the chair.

THE PRESIDENT, introducing the author of the paper, said: I think Mr Mathias may be called a real expert in this business, having spent more than thirty years in the petroleum industry. He began his scientific life with an Honours Degree in chemistry at Oxford, and joined the Shell Company in 1922 as a chemist, being concerned with the lubricating oil and bitumen side, as well as other aspects of the Company's business. He was managing director of Colas Products from 1941 until 1948; from 1948 to 1951 he was bitumen manager of Shell-Mex and B.P. Ltd. of which Company he is now general operations manager. We can look forward to a very authoritative paper.

DISTRIBUTION OF PETROLEUM IN THE U.K.—THE CHANGING PATTERN

By T. W. MATHIAS* (Fellow)

SYNOPSIS

1850–1918

The growth of the petroleum industry in the U.K. The early distribution system. The influence of the first world war on the industry.

1919–1939

Period of great development. Changes in methods of distribution with introduction of bulk. Clear-cut pattern established—tanker imports to ocean terminals—distribution by water, road, or rail to sub-installations and inland depots—thence by road or rail to consumer.

1939–1948

The Petroleum Board—the pipeline system—fuel oil expansion.

1948–1952

U.K. refinery expansion—effect on distribution—declining importance of ocean terminals—road-rail considerations—marketing trends—replanning. The increasing use of water-fed sub-installations. Modern depot layout and design. Product movement—coasters—road vehicles—rail tank cars—Customs and Excise requirements.

1850–1918

IN any consideration of the factors governing the distribution of petroleum in the U.K. it is quite impossible to overlook the historical background, and no apology is offered for commencing this paper with a brief review of the growth and development of the industry in the U.K., with particular emphasis on distribution.

* Shell-Mex and B.P. Ltd.

The petroleum industry, which has assumed such major importance in the U.K. internal economy, is of comparatively recent origin, and the earliest commercial activity recorded centred round the pioneer efforts of James Young, who was concerned with the production of paraffin from Scottish shale oil.

It is almost exactly 100 years ago that the invention of a suitable lamp for burning oil distilled from Scottish shale oil caused the first commercial activity and set the seal on the valuable technical work of Young, who has been referred to as the inventor of " cracking."

The commercial production and distribution of petroleum oil in America commenced in the sixties, and, co-incidentally with its development in that country, its use was also rapidly expanded in the U.K. Importations from America to supplement the home production were almost entirely of paraffin oil together with some lubricating oil, and the trade continued to expand with increasing rapidity until competition from gas and electricity services began to make inroads into the business hitherto enjoyed by paraffin oil. It was, furthermore, about this period that Russia became a major producing country, and with the introduction of Russian oil into the market as a strong competitor to the U.S., prices began to fall and a search for new markets began.

The Coming of the Internal Combustion Engine

It was also about this time that an event occurred which was not only to prove for many years the biggest single factor in the increased use of petroleum but was also to stimulate the oil industry to a degree unimagined by those pioneers whose main interest was in the production and distribution of paraffin oil and lubricating oils—the coming of the internal combustion engine. This had been invented about 1860, and it was shortly afterwards adapted for use in place of horses for moving carriages along the roads. It was not until the removal of the Locomotive on Highways Act in 1896 that events began to move rapidly, and from that time forward the increasing interest displayed in constructing automobiles brought with it the problem of distributing motor fuel.

At the end of the nineteenth century paraffin oil was still the main petroleum product distributed in the U.K., and although the light fractions, which had hitherto been regarded as of little importance and thrown away, were now being used as automotive fuel, the fact that in 1900 only about 2000 motor cars were on the road in the U.K. gives a measure of the significance of the problem of distribution of motor spirit.

Rapid Growth of Motor-Car Industry

From the turn of the century onwards there was a tremendous extension in the use of motor vehicles, and up to the outbreak of the first world war the business of the distributing companies was to cope with the increasing demand from the motoring community, who were introducing a major distribution problem in expecting supplies to be available anywhere over the length and breadth of the country.

This accelerated demand for motor fuel and lubricating oil naturally increased the amount of petroleum products imported into the U.K. and stimulated the development of the bulk ocean-going tanker first put into

service as far back as 1892. It also led to the provision by the importing companies of bulk storage for main products at waterside depots and installations.

During the period 1900–14 they began to transport motor spirit and kerosine in bulk by rail car to inland depots, where the product was pumped to storage and thence filled into cans for re-distribution. This is what M. B. Davy wrote in 1935 * referring to the year 1910 :—

> " Bulk Distribution
>
> " Twenty-five years ago the most important petroleum product was kerosine, with motor spirit and lubricating oil still rather in the nature of side-lines, although expanding rapidly. Imports were received in bulk at ocean installations and despatched thence to inland depots, mainly by rail tank cars. The normal method of delivering from the depots was by horse-wagons carrying a tanker for kerosine. Motor spirit was filled into two-gallon cans at the installation and larger depots, and despatched by rail to the smaller depots, whence it was delivered by the same vehicles which carried the kerosine. Lubricating oil was normally imported in barrels and despatched by rail either in barrels or drums. It was still the exception for motor lorries to be used for delivery work. The problem created by the building up of a distribution system based on the kerosine trade, which is mainly in comparatively small lots sold to a very large number of customers, and on horse transport, may be compared up to a point with that with which the railways are faced. As the radius in which a horse-vehicle can operate is restricted by the slowness of this method of transport, it became necessary to establish a network of small depots in all parts of the country, comparable to the network of small stations built by the railways. The post-war development of motor transport has enabled deliveries to be effected economically over a much wider area, but, as the capital had already been sunk in constructing the depots and the railway stations, it was found in many cases to be more economical to continue distribution from the existing small depots rather than to close the majority of them and concentrate deliveries on a limited number of depots only, which of course it would be necessary to enlarge. The railways are faced with exactly the same problem in closing small stations."

Petrol Distribution—the Last Link

As the demand for motor spirit increased, the oil companies turned naturally to the large number of cycle and repair shops and ironmongers for its distribution to establish the last link in their system, since they were already in contact with many of these people by reason of their paraffin oil trade. Gradually a nation-wide network was established by this means, and as supplies were carried in 2-gal cans and there was no minimum quantity for delivery, the different brands of the companies could be obtained from source to meet the motorists choice. Thus was established

* " Petroleum—Twenty-five Years Retrospect." London : The Institution of Petroleum Technologists, 1935.

the first major characteristic of the U.K. market, which, until recent times, differentiated it from the pattern more normally found elsewhere.

Fuel Oil: Admiralty Requirements

During this same period there was, of course, the development of fuel oil, which was at this time mainly required for Admiralty purposes. It is interesting to note that when Lord Fisher retired from the office of First Sea Lord in 1910 he had as early as 1880 seen the displacement of coal by oil as fuel for the Navy. He said: "the use of fuel oil increases the strength of the British Navy 33 per cent because it could refuel at sea off the enemy harbours. It is an economic waste of good material to keep men grilling in a baking fire hole on unnecessary labour and the use of 300 men when a dozen or so would suffice. At any moment during refuelling an oil engine ship can fight—a coal driven ship cannot; she is disorganized, the whole crew are as black as niggers and worn out with intense physical exertion. In the oil driven ship one man turns a tap. It is criminal folly to allow another pound of coal on a fighting ship."

It was in 1911, on Mr Winston Churchill's arrival at the Admiralty, that impetus was given to the extended use of fuel oil for naval requirements, and therefore alongside the expanding demand for oil products from the domestic market came the increase in demand from the British Navy. In the latter case the problem of distribution was not, however, difficult, since the Admiralty themselves set up bulk storage installations adjacent to dockyards and naval bases and received the fuel oil direct from bulk tankers carrying the material from America.

Aviation

In passing it is also interesting to recall that even in this period there was some activity in respect of aviation requirements. In 1913 the Schneider Trophy was won by France at a speed of 45·75 miles per hour, but in this case the fuel required was ordinary motor spirit, and no specifications were then in existence for the aviation spirits as known to-day.

The First World War

The first world war was the cause of a tremendous expansion in the oil industry and, although the ordinary trade in petroleum products was severely restricted, the demand on land, on sea, and in the air caused a large up-surge in the nation's requirements of imported products. The command of the major supply of the world's oil resources proved to be one of the principal causes of the allied victory, and the much repeated statement of Lord Curzon—"the allies floated to victory on a wave of oil" left no doubt in the minds of thinking people that oil was to become a major sinew of war in any future international upheaval.

As far as distribution is concerned, with the exception of fuel oil, the main products continued to be handled through the importing installations to smaller depots, re-distribution being finally effected in cans, and it was not until after the conclusion of hostilities that in 1920 the first efforts were made to change over from the package method of delivery in small lots to bulk distribution. The experience of the war had shown that considerable

economies could be effected in handling larger quantities of petroleum products of all kinds in bulk, and it became clear that if one could handle large quantities as nearly as possible up to the ultimate point of consumption vast economies were to be obtained.

1919–1939. A Period of Enormous Development

This was a period of great development within the industry, and was characterized by the implementation of the economic principle that the larger the quantity transported as near as possible to the point of consumption, the cheaper the costs of distribution. The kerbside pump introduced about 1920 was probably the most significant development accelerating the turnover to bulk, since the public were gradually educated to accept spirit deliveries through reliable metering pumps. Bulk storage depots, installed mainly at first for filling the well-known and universally accepted 2-gal can, began to be extended with the development of road bulk vehicles which drew their loads from bulk and in turn pumped into customer's tankages for ultimate transmission through metered pump to the motorist's tank. Furthermore, it became customary at this early stage of bulk supply not to deliver less than 200 gallons in bulk at a time, and the effect of this policy can be imagined on costs of distribution against the old method of sending out cans and making no provision for minimum quantities.

The bulk method of distribution was given further impetus when large commercial consumers, such as bus companies, installed their own bulk storage, and it would be a fair comment to say that no one factor contributed more to the efficiency of the distribution side of the industry than the almost complete turn-over from packages to bulk for ordinary grades of motor spirit which occurred during this period.

It has been stated that in 1900 only 2000 motor vehicles were registered for use on the roads. The phenomenal growth of the motor car can be seen when the following registrations are mentioned :—

1921 . . .	246,000
1930 . . .	1,075,000
1939 . . .	2,077,000

Motor spirit and aviation spirit consumption during the same period was :—

1921 . . .	850,000 tons
1930 . . .	3,324,000 ,,
1939 . . .	4,815,000 ,,

Kerosine, which before the first world war was the major petroleum product, was used over the same period to the following extent :—

1921 . . .	536,000 tons
1930 . . .	676,000 ,,
1939 . . .	787,000 ,,

In passing it should be emphasized that the 787,000 tons of kerosine distributed in 1939 included a substantial quantity of vaporizing oil for agricultural purposes, the natural trend clearly being for illuminating kerosine demand to decline.

The use of other petroleum products was also expanding very rapidly over the same period. Fuel oil, the consumption of which was only about 500,000 tons in 1921, had grown to 1,250,000 tons in 1939. (This excludes ships' bunkers.)

The pattern of distribution of this product reveals considerable differences from that of motor spirit in that the early development had been built up on the basis of direct supply to the consumer, who in any case required fairly substantial quantities, and so enabled comparatively large bulk drops to be effected *ab initio*. Thus a most important characteristic of the fuel oil trade is that the consumer has always been enjoined to instal adequate tankage to receive bulk quantities on a scale far more generous than that of motor spirit. The dealer has been eliminated almost entirely, and the necessity for a large chain of distributing depots has been avoided.

Bitumen was another product which profited from the introduction of bulk. Here the problem was much more difficult because of the relatively high temperatures required to raise the material to pumpable and transportable conditions, but the experience of the distributors gained in handling modest quantities of the very heavy grades of fuel oil by the use of lagged vehicles was applied to bitumen, with the result that, except for the very hardest grades, all penetration grades—and of course cutbacks—could be carried in bulk. In 1921 the bitumen consumption in the U.K. was under 50,000 tons, all imported in barrels, whereas in 1939 it had risen to nearly 650,000 tons, the vast bulk of which was worked up at home refineries from crude oil and sent to its points of consumption in rail car and bulk road wagon.

Lubricating oil was also concerned in the development of bulk delivery, and although the requirements for lubricating oil calling for large numbers of different grades in relatively small quantities restrict the scope for distribution in bulk, nevertheless, the handling of basic oils to the blenders did permit of the use of bulk wagons, either rail or road. Furthermore, the introduction of motor oil cabinets in 1925 permitted the handling of motor oils in 5-gal churns, which were carried on spirit vehicles making deliveries to garages, and hence cut out considerable distribution costs in handling barrels, cans, and tins, since the churn was filled at the depot direct from bulk storage.

Before leaving this period of expansion reference must be made to the development of the diesel engine for road vehicles. Introduced in about 1928, the diesel-engined vehicle appeared in increasing numbers on the roads, thereby accounting for nearly 500,000 tons of diesel fuel by 1939.

It is undoubtedly this period which saw the forging of all the links in the chain of commercial distribution. The pattern was quite clear cut: importations of main products were received in tankers coming from overseas at sea-board installations. These products were in their refined state, and were received into storage, where they were blended as required, or despatched by coastal vessel, barge, rail car, or road wagon to smaller depots, which in turn re-distributed the products to the consumer.

Before the second world war the distributing companies had therefore built up a considerable pattern of small depots which were the basic units upon which their system of distribution was created.

1939–1948. The Petroleum Board

Such was the position when the outbreak of the second world war occurred in 1939. It is not within the scope of this paper to deal with this period, when all supply and distribution became a function of a pooled distributing organization set up with the approval of the Government—the Petroleum Board. The energies of the companies associated with the Board were bent towards the maintenance of supplies of all types of product for the successful prosecution of the war. Costs were of secondary importance, and were of necessity subject to the exigencies of the situation which changed repeatedly with the fluctuations of the war.

The Pipeline System

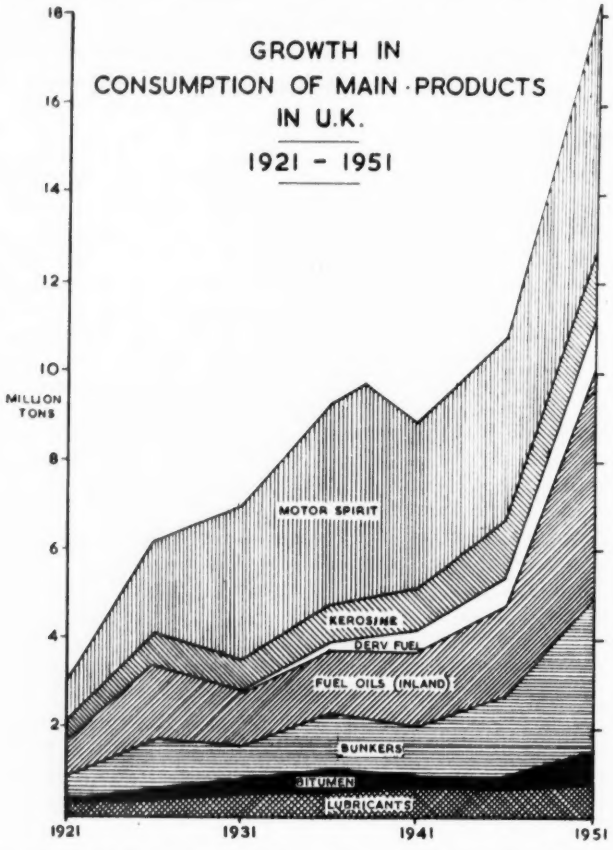
The biggest single development in distribution was undoubtedly the pipeline system, which was introduced in order to relieve the hard pressed internal transport system, then suffering from the necessity to move products from West Coast importing terminals to East Coast consumption areas. The pipelines performed invaluable service in creating ullage for replenishment cargoes at West Coast terminals, and were especially useful for large scale movements of aviation fuels, which were being consumed at what was then a fantastic rate. For reasons which will appear later, however, the pipeline system cannot be considered as a serious factor in the peacetime distribution of petroleum products in this market.

There can be no doubt that the man in the street regards the pipeline as the obvious and most sensible way of distribution on a large scale, and visitors to the U.K. who have distribution problems abroad often ask why pipeline methods of distribution are not used as a matter of course in the U.K. Economically the pipeline system can be justified only when large individual quantities are required at the consumption point to ensure effective continuous pumping from the terminal point. Furthermore, the existing pipeline system is Government-controlled, and forms a valuable contribution to the defence needs of these islands. In any programme of rearmament the pipeline must obviously be reserved for national requirements, and only when the threat of war has so far receded that it can no longer be considered a major factor can consideration be given to harnessing it to supply the industrial and consumer needs of the country. If, and when, a period of international tranquillity is reached it is possible that available techniques in handling a number of grades through the same pipeline may render consideration appropriate for the use of the pipeline for commercial purposes. But so many imponderable factors are involved that for the present, however, it can be ignored, although it must be made clear that this refers to the use of pipelines on a national scale within the general pattern of distribution—and not to the more limited commercial use, *e.g.*, refinery purposes, such as the Anglo-Iranian line from Finnart on the West Coast of Scotland, which transmits crude oil discharged from ocean tankers across the waist of Scotland to Grangemouth refinery.

Fuel Oil Expansion

The effects of the P.B. period which most impinge upon the distribution trade of the country were mainly an enormous increase in inland fuel oil

requirements (including gas oil), amounting to nearly 3 million tons increase on the 1938 level; a motor spirit requirement which, in spite of rationing, was only just short of the 1938 figure; and an increase in the demand for vaporizing oil amounting to nearly $\frac{3}{4}$ million tons, due to the very large increase in mechanization of the farms accelerated by the wartime demand for indigenous food production. In short, the consumption of petroleum



products in the U.K. had grown from 10 million tons (all figures exclude Eire) in 1939 to over 14½ million tons in 1948. Nor was this all. The period 1939–48 was very largely a time of living on the distributing companies' fat in regard to capital equipment used in distribution. Installations, storage depots, coastal craft, barges, rail cars, and road wagons, were largely the same as were in existence in 1939, and with the one exception of road wagons, little or nothing had been possible to bring into line with modern requirements the distributive systems of the country. Nothing was comparable in the U.K. to the progress made over the same period by the U.S., and distributors within the P.B. had the unpleasant experience of

seeing an ever increasing demand for their products without the availability of very much modern equipment to assist them. The break-up of the P.B. in July 1948 was, however, the signal for a further overhaul of distributing methods, and it is the effect of these changes within the period July 1948 to date with which we are now mainly concerned.

1948–1952. The Changing Pattern

This then was the situation which confronted the companies comprising the P.B. when the demerge of that body took place in July 1948. Most companies having had little opportunity of detailed planning while their staff was serving in the Forces and the P.B., reverted substantially to the 1939 pattern.

The chain of distribution was through the ocean installations in addition to the refineries, which were also operating in that capacity in so far as distribution was concerned, to the sub-installation, which was water-fed either by coastal craft or by barge, and thence finally to the depot or inland storage point, of which there were a very large number. Many of the depots were situated on railway property, and the terms of the lease included a requirement that stocking up from main distributing points should be undertaken by rail feeding. Each depot had in charge of it a superintendent, who was primarily a salesman, together with a storekeeper, a clerk to handle orders, and one or more depot hands to undertake the loading and unloading of vehicles and the general work of the depot. Even the smallest and most remote country depot had a number of vehicles based upon it by means of which distribution of motor spirit, kerosine, and lubricating oil was effected. The vehicles in question were usually of 600 to 1000 gal capacity, and a substantial number of open wagons were used, mounted with portable tanks, having space for the carriage of packages. Fuel oil was not generally handled through the depots, since, as already mentioned, from the early development of the trade it had been found more economical to deliver direct from main installations or depots specially equipped with fuel oil storage tanks. Bitumen was not handled by the depots at all, and was despatched by rail or road from the refineries whence it was produced, although some development had been made in the railhead principle where rail cars of bitumen, after steaming, were discharged direct into road tankers for re-delivery to customers.

In short, the whole of the distributive system was based on the movement of products from the ocean installation, or refinery which had storage for main products (the bulk of which were received by tanker from overseas), to the sub-installation; and a highly complicated system was evolved on the broad principle that if tenancy conditions gave freedom of choice the feeding of the small depot was done by whichever method—road or rail—gave the cheapest results.

Replanning

The demerge of the P.B. gave distributing companies an opportunity to take stock of the position and to replan the distribution of their products upon lines more in keeping with modern trends. The most important of

these was the emergence of the Middle East as an important producing centre of crude oil, and the decision of the major oil companies taken during the life of the P.B. to make the U.K. an important link in the chain of world-wide refinery operations. It is not within the purview of this paper to go into details in so far as this development is concerned, but rather to consider the effect of such a policy on the distributive system which existed in the U.K. at the cessation of the P.B.'s activities.

It will at once become obvious that the refinery expansion programme had a far-reaching effect on the distribution chain, since distributors had to face up to the decline in importance of the ocean terminals, except where such terminals had already been established at pre-war centres of refining. The considerations involved were numerous, since the role of the new refineries was planned to increase their stature to a degree hitherto unimagined and to establish the U.K. as a major refining centre. The new concept was on a vastly different scale from the old, and involved the working up at refineries of all products from crude oil received from overseas fields. The problem facing the distributor was a gradual reorientation of his distributive system phased carefully so that the increasing volume of refined products could be smoothly absorbed into the general pattern, at the same time ensuring a continuity of supply of all grades to meet the growing demand. The magnitude of the task will be appreciated when it is remembered that all this was occurring at a time when not only were materials, particularly steel, in short supply, but licences were also required for all forms of building and construction, and in parallel with this was the unfolding of the Ministry of Town and Country Planning scheme for the industrial development of the country. Furthermore, experience had shown that the small depot was becoming uneconomical due to the increasing use of road transport and with the upward trend of wage increases the more times the product was handled in its passage from main centre to the user, the higher became the distribution cost.

Road–Rail Considerations

It is at this point that some consideration could profitably be given to the problem of handling petroleum products by rail. In a paper * given by C. M. Merrick on distribution and marketing in the U.K. to the London Branch of this Institute in February 1950, the following passage occurs. Referring to road transport of petroleum, he says :—

"Fleet costs per ton mile in 1938 were virtually only half of what they were in 1928. This result was achieved by improvement in the design of vehicles, by operating them more intensively, and by employing vehicles of greater capacity. In the next ten years—from 1938 to 1948—the fall in the value of money inevitably increased costs again, but in spite of this, road vehicle operating costs are to-day well below the 1928 level, whereas rail charges were nearly 63 per cent higher in 1948 than they were in 1928."

Since this was written there has been a further disparity in favour of road costs, which is a highly significant pointer to the distributor replanning his whole system.

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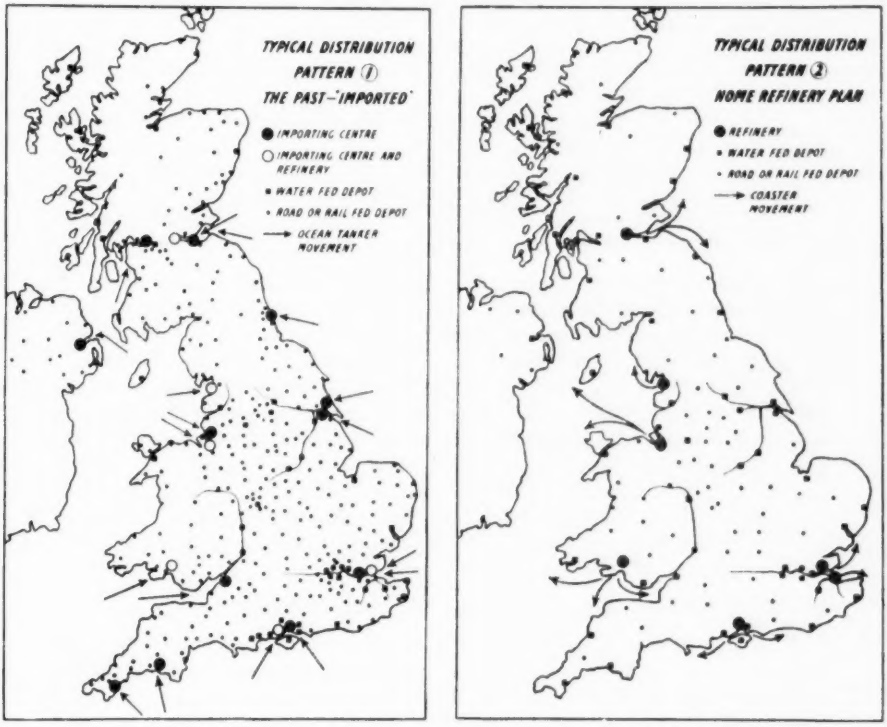
* *IP Review*, 1950, **4**, 366–72.

Marketing Trends

As this paper concerns itself with the factors affecting distribution, it is impossible to overlook certain marketing trends which have clearly emerged since the companies comprising the Petroleum Board have resumed their individualities. Apart from a steady increase in inland demand for all products, which increased from $10\frac{1}{2}$ million tons at the end of the war to more than 16 million tons estimated for 1952, there has emerged one



(*a*) Old (*b*) New

DISTRIBUTION PATTERN

development which has had a profound effect on the planning and forward thinking of the distributors. This is the scheme under which a dealer or garage owner is encouraged to take all his motor fuel from one company or a group of companies—and for certain considerations, to ensure that his requirements will be ordered in as large a quantity as possible. This scheme, which was developed fairly recently, anticipated Government approval to an early return of branded fuels in lieu of the " Pool " quality still supplied by all companies through the dealers' pumps. Unhappily, at the time of writing the Government have not yet permitted distributors to return to the system of branded grades where motor spirit is concerned, although all other products have been allowed to return to the market

under their own branded nomenclature. Nevertheless, the growth of the scheme has been of great advantage in that distribution of motor fuel has been simplified for the individual suppliers to the extent that considerably fewer retail delivery points require deliveries, and in general the average "drop" of motor spirit has increased. The effect on distribution costs has already been felt.

Factors affecting Distribution To-day

Reviewing the main factors affecting distribution since the demerge of the P.B. there are four main issues:—

(1) the concentration at the refineries of the main supply of all refined products;

(2) the diminution in the importance of the ocean terminal not associated with refinery operations;

(3) the increasing economic advantage to be obtained by a wider and more general use of road transport;

(4) the development of schemes of marketing, focusing attention on fewer dispersed deliveries and larger "drops" of motor spirit.

It is with these main factors in mind that distributors have begun to replan their distributive systems. If it were possible to start completely afresh there is no doubt that an ideal distribution plan could be effectively implemented which, having no regard to the pattern of the past, could effectively take care of the present situation with due regard for the future demands on the industry. Unfortunately it is not as simple as that, and the enormous capital investment of the past in the distributive system of the U.K. cannot be jettisoned overnight, even if it were possible to superimpose a modern economic system on the old set-up. Nevertheless, when the problem is examined in detail it is found that the two are not entirely irreconcilable and much that existed in the past can be incorporated into a modern refinery distribution plan.

The Basic Unit of Inland Distribution—the Depot

As a first step it is clear that it is of the utmost importance from an economic point of view to close down a number of relatively small depots where the costs of distribution are high, due to the on-costs of the depot themselves, the cost of double handling compared with direct delivery, and the additional transportation cost that a double handling involves. The business transacted through these depots is transferred to other depots whose economic delivery radius permits this to be done.

Having removed the "dead wood," the next step is to examine the geographical position of the refineries from which the main products are expected to flow and to ascertain the best method of transporting them most economically to the main centres of demand. As material transported in fairly large quantities by water shows a considerable freight advantage over road and rail, and as the U.K. coastline is most extensive it becomes apparent that, by making much more use of the smaller and lesser known ports, considerable savings can be made in distribution by erecting modern water-fed depots supplied from the main refineries by coaster; or where rivers and canals are available, by barges of lesser capacity. Thus can be

built up a pattern of distribution based on the cheapest method of delivery which not only serves a commercial purpose but is also of immense value to the country from a strategic point of view, since in times of national emergency considerable relief would be given to the congested rail or road systems, which would be occupied to the fullest extent on maintaining priority supplies of all kinds essential to national survival.

These water-fed sub-installations would in turn be required to feed inland depots positioned in areas of large consumption, which in turn establish the final link in the chain by supplying customer requirements in a pre-determined economic delivery radius. It is at this stage that it has been found possible to marry up the old and the new systems of distribution. Such is the network of depots which existed on the demerge of the P.B. that in nearly every case where economic planning requires an inland depot it is found that there already exists such a depot at this point, and although the replanning may demand considerable extension to the old depot to accommodate an increase in its supply functions, in most cases no insuperable difficulties prevent plans being made to adapt to modern requirements.

The Depot : Layout—Design

It is clear that distributors must give most careful consideration to the layout and design of any new construction they may require in addition to a most careful planning of their existing facilities taken into any modernized scheme. To obtain the maximum advantages in distribution costs, operational efficiency must be considered as first priority, and certain basic features must be borne in mind. These include :—

(*a*) the general arrangement of buildings with respect to yard utilization;

(*b*) the provision of office facilities that provide maximum functional use for depot personnel and proper sales facilities when such are integrated with depot functions;

(*c*) careful positioning of the loading gantry to permit of ease of loading at peak periods of a number of vehicles with minimum of delay;

(*d*) the speeding up of loading by using modern methods, such as meterized filling points with swing arms and lorry height platforms for loaders;

(*e*) the utilization of maximum sized vehicles for distribution of the product to the customer. Where road bridging is used to supply depots, the ultimate aim should be to bring the size of the sales vehicles as nearly as possible in line with the bridging vehicles to achieve maximum flexibility in working the fleet;

(*f*) the provision of facilities for routine servicing and running repairs on the vehicles based on the depot. All major repairs and overhauls should be done, by direct labour or contract, at repair shops not situated at the depots.

The foregoing considerations apply both to the new construction and conversion of existing premises, but where the former is concerned one point could be emphasized with advantage. Land acquisition should be

on a generous scale to permit of future development and extension. Distributors must have regard to the necessary demands of the business, and must allow elbow room, since the cost of future expansion is out of all proportion to the lock-up cost of an extra acre or two of land not immediately required for development.

Product Movement

With a clear-cut picture in mind of their distribution system of the future, distributors must give careful thought to the means of product movement by water, road, and rail.

Coasters.—In considering the type of vessels which can be classified as coasting tankers so far as U.K. waters are concerned, it is necessary to draw a distinction between the situation which obtained prior to the development of home refining and the present. Formerly, with a widespread chain of main ocean terminals, coasters were employed for feeding the smaller ports having restrictions on draft and often on length and beam, and in the main the ships were of under 1000 tons carrying capacity.

Under present day conditions there is, of course, a considerable amount of coasting movements from the refineries to terminals at the deep water ports, and in this trade deep-sea-type tankers are utilized considerably, but also intermediate ships of 3000 to 5000 tons capacity.

There will always continue to be a considerable volume of coasting movements for the small ports, and the vessels engaged in this business are steadily increasing in numbers. It is not proposed to discuss the larger vessels, which are in effect deep-sea ships pressed into coastal service, and the following remarks apply specifically to ships which in the main are no greater than 1000 tons capacity.

It would not be impossible to design vessels of special dimensions of considerably greater carrying capacity than the normal type of coaster to enter the shallow water ports, but it is unlikely that there will be the parallel development in the small coasting tanker that there has been in deep-sea tonnage, an example of which is the comparatively recent introduction of the super tanker of 28,000 tons deadweight or greater. These large vessels, as is well known, are built for shuttle service in the crude oil trade between the main producing areas and deep water ports in the U.K–Continent. The small tankers are required to carry finished products, and for them to fulfil their functions in the most economical and flexible manner they need to be able to carry cargoes of mixed grades without fear of contamination and generally to be of a size to enable them to enter practically all of the shallow water ports. Their carrying capacity, therefore, in relation to their dimensions is such as will give a seaworthy vessel for the relatively stormy weather around the U.K.

The existing British Flag vessels in the U.K. coasting trade were to a large extent constructed during the war under the ægis of the Ministry of War Transport—these vessels were modelled on the well-known types existing in the U.K. trade before the war. Propulsion is almost equally divided between steam and diesel motors—the former being favoured for ships which are required to handle the more viscous oils, *e.g.*, lubricants and fuel oils, in view of the ease with which steam is available for heating coils and cargo pumps.

There have been no very radical developments in the few post-war buildings of ships for the U.K. coasting trade, but in line with modern trends coasting ships are being fitted with the latest navigational aids such as echo sounding devices and radar, and nearly all the vessels are equipped with radio telephony. Within the limits imposed by their small size, accommodation for personnel is to the high standard which is usual for tanker crews.

Road Vehicles.—To anyone who has followed the development of the distribution pattern in the U.K. and in the light of what has previously been said in this paper on that subject, it will be obvious that the evolution of road transport designed for the distribution of petroleum has played, is playing, and will continue to play a very important part, although progress is being retarded by the slow rate of road improvements when compared with the rapid expansion of volume of transport by road.

At this stage of the consideration of the subject it will also be apparent that bulk petroleum road transport must be most carefully considered in the light of modern distribution requirements. As might be expected, development has very largely been conditioned by :—

(*a*) restrictions imposed by the Petroleum Spirit Conveyance Regulations (which spring from the various Petroleum Acts eventually co-ordinated in the Petroleum Consolidation Act 1928);

(*b*) the legislation governing road vehicle construction and operation in the various Road Traffic Acts;

(*c*) the general social progress of the past twenty-five to thirty years which has influenced all distribution trades, in common with industry generally.

As regards (*a*), the most important is the limitation of the size of the load, which, since 1941, has specified that the total quantity of motor spirit carried shall not exceed 3600 gal. Talks have recently been conducted between the industry and the Home Office authorities concerned, from which it is clear that objections will not be offered to an increase in the quantity to 4000 gal, and there is every reason to expect that revised regulations to provide for this advance will shortly be issued. This raises another problem which will be discussed under (*b*). It is also stated under (*a*) that no open trailer may be attached to a tank wagon, and any bulk trailer attached may not exceed 1500 gal and then not in London.

Dealing with (*b*), the regulations in the various Road Traffic Acts which govern the maximum quantities of petroleum products, other than petroleum spirit, which can be carried by road vehicle are effectively those which lay down maximum axle loads and gross laden weights. Thus it is permissible to carry up to a maximum of 22 tons gross on an individual eight-wheeled vehicle (*i.e.*, a vehicle without a trailer). This expressed in terms of gallons is 3600 gal of kerosine or approximately 3250 gal of fuel oil or bitumen. Thus permission under the Petroleum Spirit Conveyance Regulations to carry up to 4000 gal poses a problem for the vehicle designers and manufacturers to provide the extra capacity within the permissible weight limitation. The Road Traffic Act does, however, permit 32 tons gross weight with a rigid vehicle in combination with a trailer which makes it practical to carry 5500 gal of kerosine or 5000 gal of fuel oil. The rigid

vehicle and trailer is not at present in wide use, but it may well be that it will find increasing use in particular for fuel oil distribution where considerable quantities are required with regularity, such as at a modern steel works.

There has been considerable development work in the U.S.A. and the U.K. towards the construction and use of " articulated " road vehicles, and the major petroleum distributors have not been slow to realize the peculiar merits of this type of vehicle for their particular requirements.

The majority of the products handled are " seasonal," and some products more than others, but some are " black " and some are " white," so that they must be handled in separate containers. The provision of more " semi-trailer " tanks than motive units enables the latter to be continuously employed, and reduces the value of idle equipment during slack seasons, thereby reducing distribution costs.

Under (*b*) the speed limits imposed on vehicles play an important part in road distribution costs. The heavy commercial vehicles in general use immediately after the first world war were all fitted with solid rubber tyres and were usually restricted to 12 m.p.h., but the development of the giant pneumatic tyre in the period around 1930 made possible an increase in the legal speed coupled with less deterioration of road surfaces. The Road Traffic Act of 1934 made it permissible to travel at 30 m.p.h. with a commercial vehicle only if its unladen weight did not exceed 50 cwt. During the second world war this limitation was raised to 3 tons, and the greatest ingenuity has been devoted to vehicle design to get the maximum size cargo tank and/or accessories on to the vehicle to bring it within the 3 tons U.L. It has been found possible to carry up to 1200 gal on vehicles without accessories, but 1000 gal is the general pay load on vehicles fully equipped. It will clearly be appreciated that legislation which permitted all types of vehicle engaged in the petroleum distribution trade to travel up to 30 m.p.h. will have an immediate and beneficial effect on distribution costs. It is the hope of all distributors that this day may not be far distant.

The practical effect of (*c*) is to make the driving of road tankers less arduous for the driver, and generally this necessitates providing additional equipment for his comfort. The added accessories increase the unladen weight of the vehicle, making it more difficult to comply with (*b*), also tending towards a reduced pay load and from every point of view these amenities increase distribution costs. In the past thirty years " welfare " has necessitated the fitting of windscreens and enclosed cabs, instead of the open seat previously employed, additional electrical equipment, mechanically driven discharge pumps instead of hand operated ones, and within the foreseeable future cab heaters and de-misters will doubtless become standard fittings.

In planning their road distribution the companies must make use of vehicles designed primarily to comply with the regulations and must endeavour to make their dispositions with due regard to the most efficient use of the vehicles at their disposal. On runs from the main centres of production to the inland depots—bridging runs—it is clearly economical to use vehicles of maximum capacity. On redistribution to customers the aim of the distributor, through his big drop policy, is to use vehicles of as large a capacity as he can economically put into service. Geography, or

A BULK WAGON—ABOUT 1905

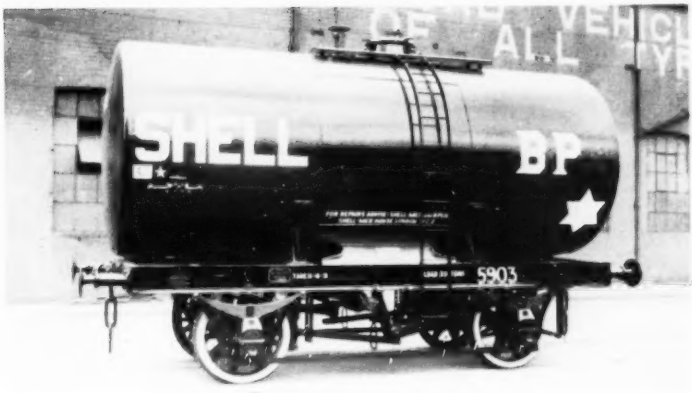
3600-GALLON RIGID TANK WAGON

[*To face p.* 140.

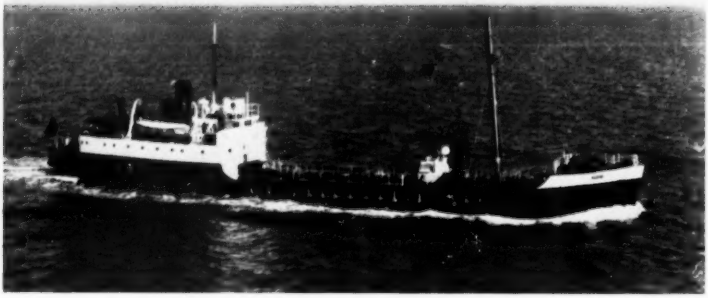
CAN DISTRIBUTION—ABOUT 1910

A BULK SPIRIT WAGON

EARLY 10-TON CAPACITY RAIL CAR



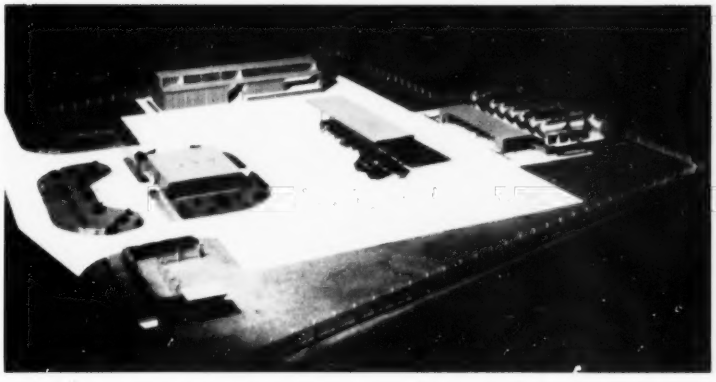
MODERN 20-TON CAPACITY RAIL CAR



Adib—a 750-ton coastal vessel

Esso Suwanee—a 250-ton coastal vessel

Esso Abingdon—a 500-ton powered barge



Lay-out of a modern depot

A MOTOR SPIRIT PUMP AT BROOKLANDS, 1907

MODERN PUMPS

rather topography, plays an important part in deciding the size and design of the vehicle in the final link of the distribution chain, but any set-back in the policy of increasing the size of the load is regarded by the industry as a problem to be overcome.

Cheapness in delivery costs is one of the most important considerations in selecting vehicles. In this connexion the steady and unmistakable trend towards the diesel-engined vehicle is one of the major factors in keeping road distribution costs on a highly competitive basis. The diesel-engined vehicle is economical with fuel, but unfortunately is more expensive in first cost, and with the present high fuel tax it can be justified only when a comparatively high annual mileage can be accomplished. The cheaper petrol-engined vehicle meantime continues to be employed extensively for local deliveries which involve low annual mileages.

The present high capital cost of road vehicles makes it imperative that there should be a minimum of idle time whilst they are in service, and shift working is a universally recognized practice within the industry.

The drive for more gallons to be delivered per annum by each vehicle is developing schemes for the cleaning, greasing, and general valeting of vehicles to be carried out overnight or in what would otherwise be "idle" time. The same principle, coupled with rising rates of pay for drivers, will probably encourage the use of other devices for reducing the time vehicles are out of service. The necessity to reduce idle time has also brought about consideration of methods to speed up loading time and turn round at the filling points. As a general rule loading at the supplying point has been by screwed connexion from the fill pipe to the vehicle, and pumping speeds rarely exceed 125 g.p.m. Distributors are now turning their attention to the open manhole filling by means of the compensated drop arm and increasing pumping speeds to 350 g.p.m. The use of the dip rod for measuring quantities is also under fire because of the slowing down of filling operations, and there is an increasing tendency to load the required quantities through meters fitted with preset devices.

At this point the use of metering at the last stage of delivery—from vehicle to customer—will have to be considered. In the U.S. much use is made of meters fitted with ticket printer heads which deliver a ticket at the time of filling. The customer accepts the ticket as proof of delivery of the quantity stated on the ticket, but so far it has not been possible to introduce this system in the U.K. There is obviously much to commend it operationally, but it must not be overlooked that such instruments are expensive, and this cost must be paid by the consumer. The education of the dealer or customer to accept metered deliveries is one obvious pre-requisite, but since in the case of the dealer this is the method by which he sells to his customers, it is reasonable to suppose that there would not be much difficulty in getting general acceptance of this method of delivery.

One of the difficulties with regard to installing meters on road vehicles is the extra weight so carried must tend to reduce pay load, but if it becomes a universal practice to make all deliveries through meters (except of course bitumen, which must continue to be sold on a weight basis), it seems logical that this difficulty will have to be overcome to complete the pattern. Some U.K. distributors are already supplying through meters, and their experience will be invaluable as an indication of future trends.

Rail Tank Cars.—Although the rail tank car is the earliest form of inland bulk distribution, the railway authorities never themselves developed this kind of vehicle, and all bulk rail transport is in ners' owwagons. All such cars must conform in design and specification to railway requirements. It is interesting to note in passing that Britain is practically the only country in which the railway authorities insist on top outlets for the carriage of low flash products, due no doubt to fear of leakage in highly built-up areas which might arise were bottom discharge permitted. The average capacity of rail cars now in use for the carriage of spirit is about 14 tons, while cars of up to 20 tons carrying capacity are used for the heavier products such as fuel oil, bitumen, etc. An interesting development has been the train-load system which permits the making up of an exclusive train of oil cars with the consequent acceleration in handling at marshalling yards and sidings. Unfortunately this has not been accompanied by a decrease in freights which might reasonably have been expected, and this, coupled with the much greater rigidity of the rail car in service, makes it difficult for this kind of traffic to be as economical as the more flexible distribution in bulk road wagons. Nevertheless, the rail car plays an important part in the modern distributive system, and the availability of rail facilities to new depots is a considerable advantage in planning the economics of the supply position.

Customs and Excise

A word about the effect of Customs and Excise requirements on distribution may not be out of place.

The tax on fuels and lubricating oils is, of course, collected by H.M. Government from the oil companies, who recover it in the price charged to the consumer. Taxes are collected at the bonded installation or depot, and moreover, are collected in advance, an assessment being made of the probable rate of withdrawal from bond at regular intervals. A fund or deposit is paid over to the Customs surveyor on the basis of the assessed rate of withdrawals, and adjustment is made against actual withdrawals from Bond at the next period for assessment. The length of the period is a matter for local negotiation—it may be weekly, four-weekly, or ten-daily.

In the pre-refinery distribution era—say 1939—bonded installations were confined to the main terminals, sub-installations, and large water-fed depots, transfers being made under bond to the latter two from the main supply point.

The rail-fed depot was not as a rule bonded, because generally it was too small, the Customs and Excise Commissioners not being prepared to grant bonding privileges to depots unless the storage for dutiable products at each was a minimum of 200,000 gallons, and again because the advantages to the distributor were not sufficiently compelling.

In determining the advantage of applying for bonding conditions it is necessary, of course, to weigh up the extra administrative costs that are inevitably associated with a bonded installation against the savings of duty on the handling and leakage losses which occur. Naturally the Customs surveyor watches very closely the scale of leakage and handling losses, and no doubt for his own purposes has some permissive tolerance, below which he will not unduly question the operations at the bonded warehouse concerned.

The reduction in the number of distribution centres and concentration at larger centres that is the fundamental characteristic of the changing pattern makes it both attractive and practicable to distribute increasingly direct to the last link in the distribution chain from bonded premises. The rate of taxation on motor fuel is now so high at 2*s* 6*d* per gallon that the saving of the duty element on leakage and handling losses is an important factor in distribution costs. As an example, it may be quoted that at the present time on motor spirit my company assess the value of drawing from refinery premises for direct issue to customer (*i.e.*, the service station or commercial consumer) at 5*s* 6*d* per ton compared with the supply of the same customer from a duty paid depot, itself being supplied from an intermediate bonded point—a pattern which was by no means unusual at one stage in our distribution history. There is an element in this figure for the value of the product, but at the current rate of duty this represents a very small proportion of it. This is a maximum figure, and for less volatile products and those subject to less formidable Customs duty the figure is substantially lower.

The use of diesel oil for road transport originally presented the revenue authorities with a problem. They did not wish to discourage its use, but at the same time it was necessary to preserve the revenues arising from the motor fuel tax. In the first stages of its use diesel oil for road vehicles was not taxed differently from any other normal oil product, other than motor spirit, and the legal definition for tax purposes was the accepted dividing line between petroleum spirit and other petroleum products, viz., tax applied to oils flashing below 73° F defined as light hydrocarbon oils. The Road Fund interests were to be preserved by a heavy licence tax on the vehicle itself. With the substantial improvement and rapid development of the C.I. engine for road transport purposes the arrangement for taxing the vehicle only soon became unsatisfactory from a revenue point of view, and so the vehicle tax was adjusted and the diesel oil used for road purposes was made to attract the same rate of tax as petroleum spirit. To-day, therefore, oils are described as being rebated or non-rebated, and motor spirit and other light hydrocarbon oils together with diesel oil for road vehicles are the only oils which fall within the latter category. All other petroleum oils are fully rebated, with the exception of lubricating oil, where the tax remains at one penny per gallon. As diesel oil has many uses other than for road vehicles it is rebated for tax purposes when required for stationary engines, etc., and unless it is drawn from bonded premises stocks must be separately maintained. In such circumstances there is much advantage in bonding premises if practicable where this product is stored, the tax being paid at the appropriate rate on issue according to the use for which the product is destined. This involves the keeping of detailed records of issues and the licensing by the Customs authorities of dealers in diesel oil for road vehicles. Users of diesel oil for road vehicles must also be licensed by the Customs and Excise authorities where they store the fuel. There is no charge for the licence, but it is obligatory and obviously imposes a number of conditions regarding the maintenance of records.

Lubricating oil is held at most distributing centres on a duty-paid basis, bonded stocks being primarily confined to the manufacturing and blending points. There are quite a lot of complications about bonding lubricating

oil products farther down the distribution chain, and in view of the comparatively minor scale of loss and evaporation and the low level of tax there is no particular advantage to be gained by an extension of the holding of bonded stocks.

Naturally certain obvious provisions for the convenience and safety of inspecting Customs officials must be made at bonded installations, and details of these are, of course, available in the various White Papers and Stationery Office issues thereon.

Aviation Fuels

Aviation fuel destined for use by the R.A.F. is controlled from the storage tank at the main installations to the time it arrives at the R.A.F. Station under a procedure agreed with the A.I.D.

Each grade of aviation fuel is isolated throughout all its movements to ensure that there is no possibility of contamination. Such fuel passes through filters of at least 180 mesh, where considered desirable, and special sampling and sealing procedure is enforced at specific points in the flow line.

Rigorous control is also exercised where aviation turbine fuel is ultimately destined for use in the jet-type aircraft, and special arrangements for cleaning are observed.

Conclusion

It has been quite impossible within the limits of a paper to do other than paint an overall picture of the growth, development, and changing pattern of distribution requirements currently in being in the U.K. There are many problems still to be solved, but these, like everything connected with this aspect of the industry, are subject to the fluctuating effects of the many factors which exert their influence on distribution. New products appear and demand specialist treatment. For example, the distribution of butane and propane in pressure cylinders brings its own problems, and the day cannot be far distant—and indeed may have already arrived—when these products will be handled in pressurized road bulk vehicles. No distributor can ever stand still : he must constantly be searching for ways and means to cheapen his costs and improve his efficiency. The petroleum industry has always had a reputation second to none for service, and good distribution, efficiently, economically, and rapidly performed can be of immeasurable service to marketing operators from this angle.

Acknowledgments

The author acknowledges the assistance obtained in preparing this paper from the following publications :—

" The Problem of Oil," by Christopher T. Brunner. London : Ernest Benn Ltd., 1930.

" Petroleum—Twenty-five Years Retrospect, 1910–1935." London : The Institution of Petroleum Technologists, 1935.

He also thanks his colleagues in Shell-Mex and B.P. Ltd., who have at all times given him the benefit of their helpful advice.

Discussion

C. Chilvers : We have listened to a valuable record of the historical development of the distribution of petroleum in the U.K. It is never an easy matter to comment on an historical paper, since it should contain statements of fact, and this paper is no exception.

Although a discussion is supposed to be controversial and provocative, I do not find very much in the paper about which one can be controversial or provocative.

I was interested in the reference to the importance of the pipeline system, which came into use during the war, but I am not sure that I agree with the author that most people in Britain would expect petroleum products to be delivered through a pipeline system. I wonder how many people really know about the pipeline which was operated by the Petroleum Board. An impression might be gained from the paper that after it came into being the pipeline system was perhaps the main method of distribution during the war. Whilst it fulfilled its function it was only a part of the very comprehensive distribution system operated by the Board. In this connexion it should be mentioned that in 1944 the railways distributed 15,000 complete train loads, averaging 300 tons per train, of petroleum products throughout the U.K. In other words, some $4\frac{1}{2}$ million tons of products were distributed through the medium of the railways, which handled, on an average, more than forty train loads per day.

The objective of the suppliers is, of course, to improve the efficiency of distribution, which in turn means reduced costs and lower prices. Mr Mathias has already referred to the importance of increasing the size of the load. What is really needed is to increase the number of gallons per man-hour. We need a maximum throughput through terminal and bulk plant and for each coaster, barge, rail car, and road tank wagon.

In the U.S. the trend to this end is to make operations more and more automatic. Mr Mathias has referred to the use of meters. Little more than a year ago I visited an up-to-date distributing depot near New York, where the loading of vehicles was just about as automatic as it can be made. On arrival at the plant, the driver of a vehicle 'phoned the control office, a large glass-walled office situated high up in the centre of the plant, and received instructions as to the loading bay and the swing arm which was to load his vehicle. He proceeded to the bay and himself inserted the swing arm, and then advised the control office by 'phone from the loading platform that he was ready to load. Throughout the operation he was under observation from the control office. By remote control from that office the correct quantity of product was delivered through a meter at the loading point, so that the driver could see the precise quantity being loaded. A duplicate meter was situated in the control office, and when the loading was completed it printed the quantity on a ticket which the driver collected. This system used a minimum of man-power, but necessarily involved very heavy initial capital outlay.

There is an aspect of distribution which is likely to be overlooked except by those in close touch with the problem regularly. The tendency is to think only of the equipment used for moving products—water-borne craft, rail cars, road vehicles, packages, etc. Adequate storage capacity and

handling facilities are essential, however, if efficient distribution is to be achieved.

Mr Mathias has referred to the importance of installing modern handling facilities at distribution depots; but that goes only part of the way. Storage must be adequate to deal with maximum size loads, and this applies not only at the supplier's end, at the bulk plants, and at terminals, but also at the customers' premises. Large drops and rapid turn-round of vehicles, whatever the type, can be achieved only if the facilities are adequate at both ends of the distribution chain. Capital spent to achieve this end must ultimately pay a dividend, not only to the supplier, but also to the consumer. Satisfactory unloading facilities are just as important as satisfactory loading facilities.

There is no doubt that much progress has been made since 1939, and if figures were available I have little doubt they would show that improved efficiency in distribution has been an important factor in limiting the increases in the prices of petroleum products generally. The petroleum industry has always had a strong sense of responsibility to its customers, the general public, and I think this has been shown not least in the progress which has been made in improving distribution facilities for petroleum products in Britain.

R. J. BRESSEY: My main interest is in the black oils side of the industry, and I have lately been trying to find a few historical facts about the early days of the distribution of gas oil and fuel oils in Britain. It is usually held that the bulk importation of fuel oil, as distinct from gas oil, started in Britain about the year 1912, but I have not yet been able to find out when gas oil was first imported in bulk and distributed in bulk within Britain. The usage of gas oil in considerable quantities by the gas industry for making carburetted water gas started, I believe, in the "naughty nineties"; * I think that development was based largely on shale oil railed down from Scotland, though gas oils from American and Russian sources were also used. I should be very interested if anyone could give any clues as to when the bulk importation and distribution of these oils started over here.*

N. L. SKILLING: The Anglo-American Oil Company was one of the largest importers of gas oil for supply to gasworks, and in 1912 was import-

* The first carburetted water gas plant in Britain was actually installed in 1890. As regards bulk imports of gas oil, G. Sell has, since the meeting, very kindly referred to some early volumes of *The Petroleum Review* and tells me that this journal recorded the following in 1899:—

		Gallons
June 24	Into Swansea for The Swansea Gas Light Co. per *S.S. Broadmayne* ex Batoum, solar distillate in bulk . . .	114,600
Sept. 1	Into Liverpool for Anglo-American Oil Co. per *S.S. Potomac* ex Philadelphia, gas oil in bulk	40,941
Dec. 8	Into Manchester for Anglo-Caucasian Oil Co. per *S.S. Balakhani* ex Batoum, solar distillate in bulk . . .	440,000
		595,541

Three years later the imports, by then described as "solar distillate (gas oil)," had increased to 26,554,090 gallons. R. J. B.

ing gas oil in bulk and supplying the Belfast Corporation gas undertaking; I am sure they were doing the same thing in England before that.

B. H. BURGESS : I should like to ask whether the author has anything to add by way of explanation to his statement that the importance of ocean terminals which are not associated with refineries is diminishing. I noticed from his illustrations that a typical distribution set-up included seven refineries around the coast.

MR MATHIAS : I think the explanation is that there were something like eighteen to twenty ocean terminals which received and stored the full range of refined products from overseas. As Mr Burgess has said, there are now seven or eight refineries which are on stream, with the result that at those particular points there will be available the full range of refined products. I think the pattern is quite clear that, as the refineries here become bigger and better and come on stream with the full range of products, there must be a concentration of that full range at those refineries, and that will mean inevitably the diminution of the importance of those ocean terminals not associated with refineries which merely imported and stored the full range of products from the other side.

M. E. THOMAS : I would ask whether, as the result of the use of meters, there is any increase in distribution losses.

MR MATHIAS : In Britain operational handling by meters is rather in its infancy. We have had meters under observation for some time, and many millions of gallons have passed through them, and we do not find that there is any appreciable increase in the loss compared with the dip stick method, provided they are serviced at regular intervals. I suggest that anyone who has any experience of meters, particularly meterized filling points, can contribute very much to the discussion, because it seems that there is an agitation in the trade itself for the companies to supply through meters and to forgo the old-established dip stick method. That is a very big and revolutionary change. There are all sorts of technical difficulties associated with the use of meters, and it is not fully proved yet that the results, so far as the trade is concerned, of supplying through meters are necessarily more satisfactory than those achieved with the dip stick.

F. H. OLORENSHAW : I have not been engaged on the refining side of your Industry, but I have the honour to be the Chairman of the National Petrol Committee of the Motor Agents' Association. Over a long period the Association has received many communications from all over the country questioning why the petrol retailer receives motor spirit in bulk, measured by dip stick, when in fact he has to deliver to the general public through a metering device—and a metering device which is subject to certain plus tolerances which may involve him in very appreciable loss.

In my own Company we handle a very large gallonage, and the loss in the course of the year amounts to many hundreds of gallons; also, during the war my Company was one of those operating under the " Pink Area "

scheme, and it has been found that retailers' losses are in an inverse ratio to the number of gallons they sell. As we pay for motor spirit C.O.D. it means that if the loss is considerable the retailers' profits will be largely affected.

MR MATHIAS : Do I gather that you on the retail distribution side are in favour of meters because you meter supplies to the general public, and you think the distributors should supply you through meters? Are you roundly condemning the dip stick?

MR OLORENSHAW : We (the M.A.A.) are receiving daily many communications on this very important matter, but I personally am not entirely convinced that delivery by flow meter would be of advantage, particularly as I am told that this takes considerably longer than by the dip stick. Incidentally, I am told that it took 16 min to deliver 500 gal through a flowmeter.

Again, if motor spirit is delivered to the retailer through a metering device, that device might very well be found on inspection to be set to give a minus quantity of up to half a fluid ounce per gallon, so possibly he might be worse off than at the present time.

On the other hand, a considerable number of motor fuel retailers say that their loss in deliveries through flowmeter is only 0·2 per cent. This is not only the loss incurred through actual deliveries to them, but includes losses through over deliveries from their own pumps.

S. D. COLWELL : I do not know whether the author would care to comment on Mr Chilvers' point concerning pipelines. I think that if we study the paper carefully we shall find that Mr Mathias has indicated that the pipeline system played a very important part in the movement of very large quantities of petroleum products in the very artificial conditions which existed during the life of the Petroleum Board. Part of its work was to clear the storages at the western terminals to enable them to receive further importation; and it is because, as has been pointed out, those artificial conditions have completely changed and we are in a position to import our requirements on each side of our country, in the east, south, and west, that the pipeline system is brought back into perspective. Whether or not pipeline systems will in future take some part in distribution, time alone will tell. I do not know whether that is a point on which the author would care to comment.

MR MATHIAS : Mr Chilvers made the point that it was not generally accepted that the pipeline was an important means of transporting petroleum products. I made the point in the paper that the man in the street rather takes that view, and I am rather reinforced in that opinion because so many people from other countries who talk about distribution seem rather astonished that we do not make more use of a pipeline system in a comparatively tight little island such as the U.K. I think it is uninformed rather than informed comment, and it was that particular aspect that I was discussing.

The other point he made, and with which I could not agree more, is to

have adequate storage at both ends of the distribution chain. Obviously we may modernize our depots and sub-installations, improve the size of our "drops," and so on, but if the customer is in no position to accept larger quantities it is of no avail. I think this business of providing larger "drops," particularly on the gasoline side, will be a major operation, because there are an enormous number of stations to be supplied, many of which have been in operation for a long time; the storage capacity at those stations is very limited, and the doubling up of their tank capacity is going to involve the expenditure of a vast amount of capital. Further, at the moment there is the question of steel supply. We may be deluding ourselves if we go in for bigger and better stations where in the last analysis we are unable to deliver the quantities. That problem is one of the most important and most difficult to solve; it is difficult to see how far it is possible to reap the benefits of improved methods of distribution.

H. S. GIBSON : Being completely uninformed on this matter, I would ask what is the general size of tank to which delivery is made. Is it not possible to deliver complete loads, if the vehicles are carrying about 1000 or 1200 gal?

MR MATHIAS : I think the answer is that at the moment a large number of stations have 500-gal and 1000-gal tanks, which may be coupled-up. Under the conditions of the supply of Pool spirit it is comparatively easy to drop a load of (say) 1000 gal, but when we get the brands back the situation will be very different, because we shall not be able to link up the tanks. I do not know what a census would reveal, but there is an enormous number of stations with tankage capacity of 1000 gal or something not much greater. I think we have in mind something greater than 1000 gal per drop. As development goes on we may be thinking in terms of 2000-gal drops and we must then obviously step up the storage at the reception end.

J. W. MARTIN : The title of the paper includes the words "The Changing Pattern." A most interesting aspect in connexion with distribution is the amount of capital represented by the equipment and facilities required. I think it would be valuable if Mr Mathias could give a breakdown, in rough figures, of the expenditure on motor transport, and so forth, for a typical marketing or distribution system.

MR MATHIAS : I think—and here some of my distribution friends in my own Company may be able to help me—if we take something like £5 million as the outlay required for a modern distribution system, the expenditure will be something like £1½ million on depots, £1½ million on coasters, and possibly £2 million, or something of that sort, on road vehicles and other forms of transport. Possibly the amount I have mentioned for depots is rather on the low side.

R. H. J. INGLE : Being new to the oil industry, I find there is a very big problem in distribution, and to my mind it could be remedied immediately without awaiting the remodelling of the whole system of distribution which

will inevitably take time and much capital. That problem is the inadequate notice presently given by many buyers of petroleum products, particularly in respect of orders from the motor spirit dealer trade. Most oil companies are faced with what I call the " fire engine " service to the roadside garage, but if the dealer could give proper forward notice of his petroleum needs, as he does when ordering any other commodity, it would be of great advantage. He does not telephone his coal merchant and say that if he does not receive delivery of a ton of coal two hours hence he will go elsewhere. That problem faces the oil industry to-day, and I think it could be remedied by improved housekeeping and closer co-operation with the industry on the part of the dealer. That would be of immediate advantage to all concerned, because distribution could be more effectively and economically planned, and that planning would reflect itself in the cost of distribution and, therefore, in the cost of the commodity to the user.

R. J. BRESSEY : The question of refinements in service is very intimately tied up with that of storage capacity. In the fuel oil trade we currently recommend that the user should have storage capacity " equivalent to the quantity specified for the delivery plus a reserve equal to a fortnight's supply at maximum rate of oil consumption per week, or three weeks' supply at maximum rate of oil consumption per week, whichever is the greater." Users who adopt this recommendation do not need nor expect a " fire engine " delivery service, as they can order in advance on a rational system, and it does not usually matter to within a day or two when the delivery is made. If, on the other hand, the user has inadequate storage he will almost inevitably expect a " fire engine " service, especially if his requirements are liable to fluctuate rather widely or in a way which he cannot accurately predict. If, for example, he has a 500-gal tank to deal with requirements varying from say 50 to 200 gal a day, he is bound to require small deliveries to " top-up " his tank at irregular intervals and very short notice in order to avoid running out of supplies, and this can too soon and too easily degenerate into a demand for, and complete dependence on, a " fire engine " delivery service.

MR INGLE : I would like to give a very simple answer to Mr Bressey that according to my information the average storage at the garage in Britain is about 1750 gal, whereas the average " drop " by the Company I represent, in the case of motor spirit, is round about 500 gal. Thus, while I fully support the need for adequate storage at the garage, I do suggest that even to-day many possess sufficient reserve of tankage to give much more reasonable notice of their requirements.

MR BRESSEY : I am trying to help my friend ! I would like to ask if that 1750 gal is the average total storage of the site or the average size of individual tank ? That seems to me to make a great deal of difference, especially when different brands are involved.

I. D. COLWELL : I think the real answer is that we want both. I am perfectly convinced that an improvement in storage facilities at the average site is something of which all distribution companies can take advantage.

But the point is that, even with the storage available and allowing for the exceptional demands from time to time, there is still quite a lot to be done in the ordinary routine day-to-day business to anticipate requirements, rather than wait until stock is reduced to about 150 gal or so and then ring for the " fire engine " service. I think that, with a little intelligent co-operation beforehand, quite a lot of notice can be given which will enable the distributing companies to plan in advance and to work a planned route and full loads.

C. Rees Jenkins : The " fire engine " service has come about because of the very fine distribution service which the major companies have given for very many years. Some twenty years ago I was depot superintendent of a county depot belonging to the firm from which the speaker comes; I found there that people were asking for the " fire engine " service, and in fact within very narrow limits I was in a position to give it.

I tackled one man at a time when we were suffering very serious competition from companies operating from the main ports and quoting cheaper prices than ours, but they were carrying their loads very much greater distances by road. I pointed out to him that he could not telephone those companies and obtain deliveries of their gasoline within an hour, and I asked him why he expected such service from me. He said he was aware that he could not get quick delivery from them and, indeed, he had to give them five days notice. " But," he said, " their petrol is a halfpenny cheaper, and so I do it."

Directly a man is able to get the " fire engine " service he will take it, if he wants a branded spirit. On the other hand, if he wants something cheaper he is prepared to think ahead, and if it is the only way in which to get motor fuel he will think ahead. The reason the quick service is needed is not so much that people expect it, but that it is there. If they cannot get it they will be content to send postcards.

Mr H. W. Hastings : I understand that in the U.S. the delivery of gas oil to domestic heating users is done overnight. Is it done on the " milk round " basis, by just topping up tanks prior to the cold weather, or on a regular routine system ? If on a " milk round " basis, how does it affect the price schedule ? Presumably the suppliers sell on the basis of a minimum quantity per delivery. Have you any information on that ?

Mr Mathias : I believe that in the U.S. deliveries are made on the " milk round " basis, if you mean by a " milk round " the delivery of the oil at the option of the supplier or at the time he wishes to deliver it. I am not an expert on U.S. oil distribution, but I think they have a system which they call " absentee delivery," whereby, by means of a safety gadget, which has a whistle or something of that sort, they couple up and put in (say) 200 gal of domestic oil, and then put through the letter-box a note showing the meter reading, or whatever system is used for measurement, as an invoice.

But the point is that if the distributor can arrange to route his vehicles for the delivery of small " drops " at times when he has vehicles available, and can do it at his rather than at the customers' option, it is obviously a

very attractive proposition. The " milk round " means, I think, that the supplier can top up at a time when it suits him best, and is not on call, as in the case of the " fire engine " service.

THE PRESIDENT: Personally I have found this paper most interesting. I see a number of friends here who are at the production end of the business, and I think they will agree with me that it is interesting indeed to hear something of the final link in the long chain stretching from the producing well to the filling station.

It is of special interest to hear of the way in which costs change. At the producing end we think in very large sums covering large schemes. Our unit is probably never less than 1000 tons of oil, and sometimes it goes up to millions of tons. But in this distribution sphere we are down to very small quantities, where the incidence of cost is extremely important. After all, a penny per gal represents 30*s*. per ton and a change of 30*s*. per ton is enormous; one can very easily appreciate the importance of the various links at the distribution end of the chain as affecting costs. Items such as increased storage capacity, the organization of transport to allow the full capacity of the vehicles to be used, and the use of vehicles for as many hours of the day as possible, can react much more on the financial results obtained than can considerable economies and improvements in efficiency at the producing end. After all, it is the distribution system which takes the product to the customer and brings in the money which feeds all the way back to the producing end. It is, therefore, one of the most important parts of the petroleum business.

I am sure you will all wish to join with me in thanking Mr Mathias for having presented this paper, for having explained to some of us, who did not fully appreciate the problems of distribution, how it is organized, and for having provoked a stimulating discussion.

(The vote of thanks was heartily accorded. Mr Mathias briefly expressed his appreciation.)

ACID TREATMENT OF SHALE GASOLINE

PART II. SOME TREATMENT REACTIONS

By Geo. E. Mapstone (Fellow), J. S. Durham, W. J. Hogan, B. Nartsissov, G. Nottes, and J. Szewczyk

Summary

The influence of treatment temperature, amount, and concentration of sulphuric acid and of various addition agents has been examined, and it is shown that as the temperature increases the desulphurization efficiency improves independently of but parallel to the treatment loss. This effect is experienced with even mild acid treatment, and may be due to the alkylation of thiophenes with olefins and the removal of the alkyl thiophenes in the re-run bottoms. Hydrofluoric acid, aldehydes, acetone, and copper sulphate appear to be without effect on the results of the treatment.

Clear octane numbers first increase and then decrease with increasing severity of treatment. This suggests that a mild acid treatment removes some "pro-knock" compounds, and the removal of high octane number aromatics and olefins occurs with more severe treatment.

An attempt to apply the aminomethylation reaction of thiophene for the selective removal of thiophenes was only partially successful, but the results indicate that approximately only 0·02 per cent of sulphur is present as thiophenes which have a free α position and are therefore amenable to the reaction. It is possible that aldehydic-oxidation products formed in the gasoline during storage prior to acid treatment, together with the tar bases present, have a small effect in increasing the efficiency of the acid treatment process.

An examination of the spent neutralization caustic wash which follows the acid treatment suggests that the surface active acids formed during treatment are principally alkyl sulphuric acids and are produced to the extent of approximately 1 per cent of the gasoline or 2 per cent of the olefins present.

Distillation of the spent caustic solution yields gasoline and oil, both of which contain alcohols. The gasoline also contains small amounts of ketones from which methyl-ethyl-ketone was isolated and identified.

The high sulphur content of re-run bottoms from acid-treated cracked shale gasoline indicates the presence of approximately 25 per cent of sulphur compounds, while the high specific gravity suggests the presence of poly-cyclic aromatics, probably from the oxidation of *cyclo*alkyl aromatics formed initially. The average molecular weight of the bottoms indicates their formation by the condensation of an average of two molecules of gasoline.

On cracking, the sulphur concentrates in the gasoline fraction and appears to be largely thiophenic and at the same time a large proportion of tar acids becomes caustic extractable. These observations are in agreement with the thermal dealkylation of alkyl thiophenes and alkyl phenols formed by the condensation of these materials with olefins during the treatment process.

Introduction

During an investigation into the factors influencing the efficiency of the acid treating of cracked shale gasoline, laboratory work was carried out and helped to elucidate some of the reactions occurring during the treatment process.

It was also desired to determine the effect of a simple acid treatment on the octane rating and lead susceptibility of crude shale naphtha. The latter is usually thermally reformed to raise the octane number, and is then

refined in admixture with the stabilized pressure distillate from the cracking of the crude shale oil.

Thiophenes are among the sulphur compounds most difficult to remove from gasoline by any of the usual treatment processes, and appear to be present to a large extent in cracked gasolines, particularly shale gasoline. Hartough and his co-workers have studied the chemistry of thiophenes, and their aminomethylation reaction [11–17] appeared to have promise for the selective removal of thiophenes from gasoline. Briefly the reaction involved is a type of Mannich reaction in which thiophene, formaldehyde, and ammonium salts condense together to give 2-aminomethyl thiophene or 2-thienylamine. This amine is acid-soluble, and could be removed completely if the reaction were quantitative. In the presence of excess formaldehyde, the amine forms 2-thienyl formaldimine which may react with further thiophene to give di(2-thienyl)methane [14] or which may polymerize to give acid-soluble, alkali-insoluble resins.

An attempt was made to apply this reaction to the desulphurization of shale gasoline as an adjunct or alternative to the conventional acid treatment.

After gasoline has been acid treated it is customarily given a water wash and finally a caustic treatment to remove residual traces of acid. The optimum initial sodium hydroxide concentration was 1 lb per gallon, and if more than this amount of alkali were neutralized, emulsification troubles were experienced. Since this was obviously due to the presence of a large proportion of organic derivatives of sulphuric acid, it was decided to examine the spent neutralization caustic wash to see whether the reactions occurring during the acid treatment process could be explained.

The relative significance of the different acid treatment reactions varies with the proportions of the various gasoline constituents and the conditions of treatment. Hence, it was decided to make a preliminary survey of the re-run bottoms obtained from the acid treatment of a cracked shale gasoline so as to throw some light on the reactions involved and to extend previous knowledge of the composition and mode of formation of the distillation residue with a view to providing a basis for possible by-products.

Experimental

Effect of Treatment Conditions

For laboratory experiments the material used was stabilized pressure distillate [1, 2] after being topped to approximately 70° C (Table I).

Table I

Examination of Untreated Gasoline

Sp. gr. at 60° F	0·761
Distillation, ° F :—	
I.B.P.	137
10%	188
50%	264
90%	337
F.B.P.	371
Total sulphur, % w	0·33
Tar bases, % vol	approx 0·5

The treatment was similar to U.O.P. method H–97–40 [3] but using a 200-ml charge in a 750- or 500-ml three-necked flask. The requirement

TABLE II

Examination of Acid Treated Shale Naphtha

Treatment	Nil				5½ lb/br				6½ lb/brl				7½ lb/brl			
Sp. gr. at 60° F	0·735	0·741	0·744	0·756 *	0·728	0·730	0·734	0·741	0·725	0·732	0·733	0·757	0·725	0·728	0·732	0·734
Distillation, ° F :—																
10%	199	208	212	202	170	192	190	196	185	188	192	201	186	188	195	196
50%	226	241	249	260	213	226	229	246	213	224	229	240	216	227	231	239
80%	251	273	282	310	243	259	269	290	240	260	268	284	244	260	262	282
F.B.P.	319	347	357	430 *	312	336	327	350	310	337	331	354	319	326	336	343
M.M. Octane Number :—																
Clear	54·4	51·6	50·5	48·0 *	56·5	54·0	54·2	51·0	55·7	52·5	51·0	50·7	52·0	50·7	50·4	48·3
1·5 cc TEL/gal	62·4	59·5	—	—	65·4	62·6	63·6	60·3	66·0	62·6	61·4	59·5	64·3	62·3	61·0	60·2
2·5 cc TEL/gal	64·8	61·8	—	—	67·2	64·4	65·4	62·9	67·8	64·4	64·2	62·0	66·8	65·0	63·6	63·7
3·5 cc TEL/gal	68·0	64·3	—	—	70·4	67·2	69·3	66·4	71·2	68·0	67·4	66·0	70·5	68·7	66·6	66·6
Total sulphur, % w	0·28	0·28	—	0·32 *	0·11	0·13	0·14	0·17	0·07	0·09	0·07	0·10	0·03	0·05	0·05	0·06
R.V.P., lb	—	—	—	—	—	—	2·4	1·6	—	2·6	—	1·2	—	—	—	—

* Raw naphtha as charged to the treatment plant. The raw naphtha normally has a distillation "tail" and the octane rating of the higher boiling fractions is somewhat higher than that of the corresponding crude oil fractions of the crude shale oil because of the inclusion of some of the more aromatic light ends of the absorption oil.[10]

of sulphuric acid was calculated to room temperature, 30°, 21°, and —5° C being chosen for treatment temperatures. In each case, after mixing had been accomplished, the gasoline was separated from the acid sludge, washed with 100 ml water, next with 40 ml of 10 per cent caustic soda for 5 min, and then twice with 50 ml of water for 1 min. Care was taken to recover all gasoline from any emulsion formed during washing. The decrease in volume of refined material was recorded as treatment loss. Sulphur content was determined on the treated sample, and 100 ml were redistilled from a 250-ml flask fitted with a 6-inch column packed with jack chain. The distillate was measured, washed with caustic soda, and analysed for total sulphur content. In special cases the distillate was analysed prior to caustic washing, and in each case total sulphur content was found to be 0·01 and 0·02 per cent less before washing. At present no explanation can be advanced to explain this change, which is in the opposite direction to that expected. During distillation of some samples which had received heavy treatment, the liquid remaining in the flask turned green when vapour temperature reached 210° to 220° F. Gasoline treated at —5° C was from pinkish yellow to canary yellow in colour in contrast with the deep yellow to yellowish brown colour of that treated at the higher temperatures.

Effect on Octane Rating and Lead Susceptibility of Shale Naphtha

For this part of the work crude shale naphtha was charged to the Alfa Laval acid treatment plant [1,2] at a rate of 1650 gal/hr, and after stabilized conditions were reached samples were taken representative of treatment with 5½, 6½, and 7½ lb sulphuric acid per barrel. These samples were neutralized and re-distilled using a 1½-inch dia column packed with ⅛-inch glass beads. Four distillates were prepared with cut points of 275°, 300°, 325°, and 350° F and were further neutralized. Inspection data including motor method octane number (clear and with 1·5, 2·5, and 3·5 ml TEL/I.G.) were determined (Table II).

Removal of Thiophenes

Attempts were made to remove thiophenes from gasoline with formalin and with ammonium chloride and sulphate (Table III) with and without

TABLE III

Treatment of Gasoline with Formalin and Ammonium Salts

Results as sulphur content per cent by weight; average of duplicate analyses

	Time of treatment	
	30 min	6 hr
Original sample	0·274	0·274
100 ml treated with 3 ml formalin and		
(*a*) 1 g ammonium chloride	0·268	0·257
(*b*) 1 g ammonium chloride plus 1 ml 10*N*-hydrochloric acid	0·262	0·302 *
(*c*) 1 ml 15*N*-ammonia	0·270	0·247
(*d*) 1 ml 15*N*-ammonia plus 3 ml 10*N*-sulphuric acid	0·277	0·241

* High result probably due to hydrochlorination of some olefins.

excess acid. All showed a slight desulphurizing action. Amines gave similar results (Table IV), hydroxylamine giving the maximum decrease in sulphur content of treated gasoline.

TABLE IV

Treatment of Gasoline with Formalin and Amines

Results as sulphur content per cent by weight; average of duplicate analyses

	Time of treatment	
	15 min	6 hr
Original sample	0·274	0·274
100 ml treated with 3 ml formalin and		
(*a*) 1 g hydroxylamine hydrochloride	0·256	0·257
(*b*) 2 ml phenylhydrazine	0·269	0·276
(*c*) 1 ml phenylhydrazine plus 3 ml 10*N*-sulphuric acid	0·288	0·280
(*d*) 3 ml aniline	0·279	0·272
(*e*) 3 ml aniline plus 10 ml 10*N*-sulphuric acid	0·282	0·280

Because of the small decrease in sulphur content obtained, experiments were carried out on commercial benzole, of which the sulphur content was essentially thiophene. In this case treatment with formalin or ammonia and ammonium chloride gave increased desulphurization (Table V), while

TABLE V

Treatment of Benzole with Aldehydes and Ammonia *

Test No.	NH_3 conc	NH_4Cl	Aldehyde		Treatment	Time	Sulphur, % w	
			Amount	Type			Total	Decrease
1	Nil	Nil	Nil	—	Nil	Nil	0·367	—
2	1 ml	Nil	3 ml	Formalin	Shaken cold	15 min	0·216	0·151
3	1 ml	Nil	3 ml	Formalin	Shaken cold	2 days	0·332	0·035
4	Nil	1 g	3 ml	Formalin	Refluxed strongly	30 min	0·235	0·139
5	Nil	1 g	Nil	—	Refluxed strongly	30 min	0·374	—
6	Nil	1 g	2 ml	Benzaldehyde	Refluxed strongly	30 min	0·224	0·150

* After treatment of 100 ml benzole as above, it was washed with dilute hydrochloric acid and water and dried by filtration before determining the sulphur content. In refluxing experiments a dry ice-cooled condenser was added to the water condenser to prevent loss. Results are average of duplicate analyses.

substitution of benzaldehyde for formalin and metaformaldehyde or metacetaldehyde decreased the sulphur content by approximately 50 per cent (Table VI). The substitution of pyridine sulphate for the ammonium salt gave the maximum sulphur decrease (from 0·248 to 0·056 per cent weight), and the pyridine homologues recovered from the cracked shale gasoline gave a significant though smaller decrease (Table VI). After the preliminary unsuccessful work on shale gasoline, the catalytic influence of sulphur dioxide on the reaction had been reported together with the effect of aminomethyl sulphonic acids.[17] Additional work was therefore carried out along these lines (Table VII) when, after further redistillation, the samples showed a small but definite decrease in sulphur content. A reddish brown resin was formed during these tests, and in alkali solution was similar in odour and colour to the neutralization caustic wash from the plant.

TABLE VI

Treatment of Benzole with Different Aldehydes

100 ml treated with		Residual sulphur content, % w (average of duplicate analyses)		
NH_4Cl, g	Aldehyde,* g	Metaldehyde	Metaform-aldehyde	Formalin
Nil	Nil	0·248	0·248	0·248
0·2	0·2	0·116	0·124	0·140
0·4	0·4	0·114	0·129	0·137
0·6	0·6	0·120	0·152	0·121
0·8	0·8	0·132	0·131	0·133
1·0	1·0	0·116	0·104	0·118
Pyridine † 1·0 ml formalin				0·056
Shale tar bases †‡ 1·0 ml formalin				0·138

* 3·0 ml formalin taken as 1·0 g of aldehyde.
† 0·2 ml pyridine or shale tar bases + 0·3 ml 30% sulphuric acid.
‡ Shale tar bases isolated from cracked shale gasoline.

TABLE VII

Treatment of Gasoline with Aminomethylsulphonic Acid

Results as per cent sulphur by weight; average of duplicate analyses

Reagent	Treatment	Treated	After caustic wash	After dist to 375° F
Nil	Nil	0·333	—	—
A	Refluxed 1 hr	0·350	—	0·326
A	Stood together overnight	0·343	—	0·321
B	Refluxed 20 min	0·319	0·320	—
B	Stood together overnight	0·367	0·364	—
B	Refluxed then stood overnight	0·409	0·367	—
B	Stood overnight then refluxed with sodium hydroxide	0·382	—	0·322

Reagent A. 3 g sodium sulphite, 1·1 g ammonium chloride, 1·6 ml formalin and 2·0 ml conc hydrochloric acid added to 250 ml gasoline.

Reagent B. 2·5 g aminomethyl sulphonic acid and 2·0 ml formalin added to 250 ml gasoline. The aminomethyl sulphonic acid was prepared by method B of Hartough *et al.*[17]

Neutralization—Spent Soda Examination

Both free and total alkali in the solution were readily determined by titration with acid and the surface active organic acids by the method of Barr *et al.*[18] No direct method was found for the determination of sodium sulphate, the most satisfactory method being the analysis of the solution before and after use, the sodium sulphate formed being calculated by difference. In this way, approximately 60 per cent of the absorbed acid was estimated to be sulphuric acid, the remainder being organic acids.

Eighty to ninety per cent of the free acid remaining in the gasoline leaving the separator was removed by the water wash before contact with the caustic wash, approximately 40 per cent of the removed acids being organic. Since the proportion of organic acids to sulphuric acid in the

gasoline was the same before and after the water wash, they were probably in very fine suspension rather than dissolved in the gasoline.

On distillation of the spent caustic solution, about 3 per cent of dissolved gasoline was liberated.

Acidification of the solution with an equal volume of 30 per cent sulphuric acid caused approximately 20 per cent of a nearly black oil to separate. This oil smelt strongly of acid sludge and sulphur dioxide, and dissolved readily and completely in water, from which it was largely reprecipitated by the addition of 30 per cent sulphuric acid.

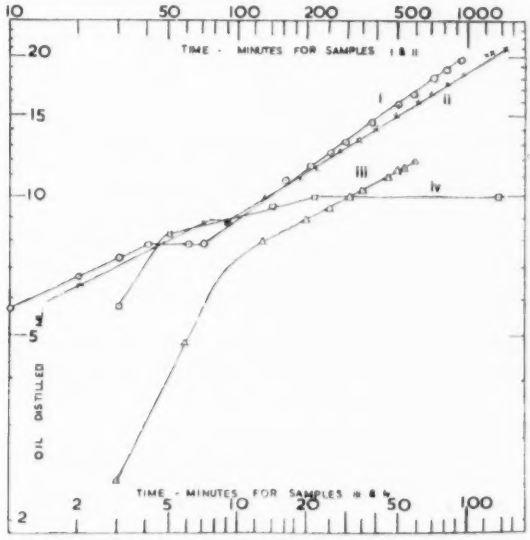


FIG 1

RATE OF HYDROLYSIS OF SPENT CAUSTIC

Samples (i) and (ii) were duplicate analyses on a fresh 250-ml sample of the neutralization caustic. These solutions were acidified with 30% vol sulphuric acid after 90 and 70 min respectively.

Samples (iii) and (iv) had stood for two to three weeks before testing. The tests were carried out using the crankcase diluent equipment IP 23/45(T).

When the spent neutralization caustic solution was refluxed, several per cent of an oil were evolved slowly. With three of the four tests shown (Fig 1) the volume of oil distilled (IP 23/45(T)) first increased and then remained constant. Acidification of the solution then promoted the distillation of further oil. Samples which had stood for some time before distillation gave more oil and at a faster rate than those samples which were distilled when fresh. When the solution was acidified prior to refluxing, the rate of oil evolution increased, indicating that some of organic acids initially present in the solution hydrolysed or decomposed on standing.

On direct distillation without reflux, the solution boiled steadily, and a little oil, consisting mainly of gasoline, distilled over very quickly. After approximately half the solution had distilled, further heating frequently

caused charring. The distillation residue was a black, viscous liquid which deposited a large quantity of lustrous crystals ($Na_2SO_4,10H_2O$) after cooling and standing for a while. The results of one such test are presented in Table VIII.

TABLE VIII

Distillation of Spent Caustic Solution.

	Original liquor	After 50% distilled off	Mother liquor from crystallisation	Acidified then 50% distilled off
Surface active agent as sodium octyl sulphate lb/gal . .	1·32	2·65	2·91	1·65
Alkalinity as NaOH lb/gal .	0·32	0·70	0·62	—
Total solids lb/gal . . .	3·25	6·2	6·8	—

Rendering the solution just acid to methyl orange before distillation gave a much greater yield of oil at the expense of the surface active agent.

Careful evaporation of the solution to dryness on a water bath gave a puce-coloured, putty-like solid with a soapy feel, careful drying of which gave a dry powder which decomposed with blackening and evolution of sulphur dioxide on standing overnight at 95° C. Carbonization of the residue gave a heavy yellow malodorous oil which represented approximately 12 per cent of the original solution.

During larger scale (4-litre) distillation of the spent caustic solution, the first oil distilled was water white, but later the colour changed to pale yellow (Table IX). These oils were bulked and distilled to 360° F. This

TABLE IX

Properties of Oil Distillates from Spent Caustic

	Oil from reflux tests	Colourless distillate	Yellow distillate	" Gasoline "
Sp. gr. at 15·5° C . .	—	0·774	0·909	0·792
Distillation, ° C :—				
I.B.P.	82	68	82	72
5%	121	89	127	91
10%	138	96	151	96
30%	165	112	178	119
50%	188	127	198	132
70%	216	143	216	147
90%	278	170	230	169
95%	—	182	241	181
F.B.P.	297	208	271	202
% over . . .	94	98	99	98
Sulphur, % w . . .	—	—	—	0·18
Octane No., M.M. . .	—	—	—	65·6

distillate was principally gasoline and was subjected to further examination.

The fraction of the oil distilling above 182·5° C (360° F) was red-brown in colour and of 0·910 sp. gr. at 15·5° C.

Because of the probable presence of alcohols in the oil from the hydrolysis of alkyl sulphates in the spent caustic, an attempt was made to esterify this fraction with palmitic acid and with phthalic anhydride. Positive tests were obtained for alcohols on both the " gasoline " fraction and the

heavier oil with ammonium ceric nitrate,[21] but no quantitative results could be obtained.

On distilling the " gasoline " fraction (Table X) the first four fractions

TABLE X

Fractionation of Oil Distillate from Spent Caustic

Cut no.	Range, ° C	Vol, %	Ketones *	M.p. of * deriv, ° C	Test with Schiff's reagent	Dr test
1	40– 90	13·5	+ve	114	+ve	Sour
2	90–100	16·5	+ve	133	+ve	Sour
3	100–105	9·0	+ve	124	+ve	Sweet
4	105–110	9·0	+ve	122	+ve	Sweet
5	110–120	13·0	+ve	133	+ve	Sweet
6	120–130	13·5	−ve	—	−ve	Sour
7	130–140	10·0	−ve	—	−ve	Sour
8	140–150	7·5	−ve	—	−ve	Sour
9	150–	8·0	−ve	—	−ve	—

* Tested with 2 : 4-dinitrophenylhydrazine and m.p. of derivative.

(to 110° C) were colourless, but the colour of subsequent fractions increased through pale yellow to a deep yellow and the residue was very dark.

The first five fractions gave a yellow precipitate when treated with 2 : 4-dinitrophenylhydrazine. The precipitate from the first was identified as that of methyl-ethyl-ketone by its melting point and its failure to depress the melting point of an authentic sample of methyl-ethyl-ketone-2 : 4-dinitrophenylhydrazone.

Examination of Re-run Bottoms

The IP 123 distillation ranges of two different samples are given in Table XI.

TABLE XI

Distillation of Re-run Bottoms

Sample	Bottoms A		Bottoms B		Steam distillate of bottoms (93%)
Distillation method	IP	Rapid	IP	Rapid	Rapid
Distillation, ° C :—					
I.B.P. . .	134	136	104	184	100
5% . .	204	160	158	228	197
10% . .	231	223	214	247	225
20% . .	259	262	241	265	267
30% . .	267	269	230	278	275
40% . .	276	276	238	294	282
50% . .	284	281	238	305	291
60% . .	—	291	—	322	300
70% . .	—	314	—	340	318
80% . .	—	340	—	350 +	335
90% . .	—	370	—	—	350
F.B.P. . .	285	370	—	350 +	352
% over . .	55	90	—	85	92
Approx mol. wt.*	—	195	—	—	—

Steam distillation of the re-run bottoms with auxiliary heating of the oil to 186° C gave a pale yellow oil and a black residue insoluble in methanol, only slightly soluble in gasoline, but readily soluble in benzole or carbon tetrachloride, suggesting an asphaltic composition.

To obtain large quantities of various fractions, 3 litres of the re-run bottoms were distilled, the distillate being collected in 20° C and later in 10° C cuts. Yield and properties of the various fractions are given in Table XII.

TABLE XII

Examination of Fractionated Re-run Bottoms

Fraction	% vol	Sp. gr. at 60° F	% w sulphur	Bromine No.	Colours with hydrochloric acid			
					5*N*-acid		7*N*-acid	
					Oil	Acid	Oil	Acid
Original	100	0·96	4·52 *	10·45	—	—	—	—
20°–140° C	0·20	0·812	0·49	—	Greenish yellow	Scarlet	Greenish yellow	Intense red brown
140°–160° C	0·13	0·836	1·11	—	,,	,,	,,	,,
160°–180° C	0·30	0·842	1·45	7·54	,,	,,	,,	,,
180°–200° C	0·53	0·861	1·88	9·33	,,	,,	,,	,,
200°–220° C	0·87	0·867	2·28	9·19	,,	,,	,,	,,
220°–240° C	2·53	0·873	3·04	5·38	,,	,,	,,	,,
240°–260° C	7·00	0·887	3·47	7·32	,,	,,	,,	Brown
260°–270° C	9·53	0·906	4·20	7·12	,,	,,	,,	,,
270°–280° C	8·83	0·916	4·65	9·25	,,	,,	,,	,,
280°–290° C	20·90	0·929	5·18	10·37	,,	Olive green	,,	Brown-green
290°–300° C	23·16	0·940	4·69	8·02	Dark yellow	,,	Brown	,,
300°–320° C	18·33	0·951	3·70	10·6	Brown	,,	Dark green	,,
Residue and loss	7·69	1·3 †	6·14 †					

* Sulphur in ash in the form of inorganic sulphates was 0·55% w.
† Calculated, neglecting the loss of hydrogen sulphide and other gases during the distillation.

Total sulphur content was determined by the quartz tube method (IP 63/42(T)), except that for the sample boiling up to 140° C the lamp method (IP 62/42) was used. Neither the crude re-run bottoms nor the distillate fractions corroded a polished copper strip at 100° or 150° C. The first traces of copper corrosion (*i.e.*, darkening of the copper strip) were observed with the 300° to 320° C fraction when heated to 270° C.

All distillate fractions were sweet to doctor test, showing the absence of mercaptans. No mercaptans could be detected in the distillate after reduction with zinc dust and acetic acid, indicating the absence of disulphides.

Gibbs test for phenols [23] was positive with all distillate fractions, while Cotton's test [23] was slightly positive with only the last fraction (300° to 320° C). Guareschi's test [23] showed a strong amber coloration not mentioned in the available literature on the subject.

The bromine numbers (Table XII) of the original sample and of the distillate fractions were determined by the modified method of Francis.[3, 24]

An attempt was made to eliminate olefins by mild bromination, *i.e.*, cooling and low concentrations (20% in CCl_4) of bromine. After approximately 20 ml of the bromine solution had been added to 100 ml of the fraction, the reaction mixture turned greenish black and evolved fumes of hydrogen bromide energetically. Further addition of the bromine solution resulted in a total blackening of the mixture and its resinification. As the

object of the experiment was the elimination of olefins without any polymerization, it was discontinued.

All the distillates gave colours if contacted with acids and, since nitric and sulphuric acids reacted further with the fractions, the colours obtained with hydrochloric acid were examined.

On shaking 2 ml of oil with 2 ml of 5*N*-hydrochloric acid, intense colour changes (Table XII) were observed within 5 to 10 min in the acid and oil layers. They remained stable for 1 to 2 hr, and finally changed into an indefinite dark greenish brown in both layers.

In order to check the presence of polycyclic aromatics in the re-run bottoms they were treated with picric acid to precipitate the picrates, but in no case was any precipitate formed, although on standing, a few small crystals were formed. Since this trace of precipitate may have been picric acid deposited from the saturated solution, it was not further investigated. Strong cooling with dry ice failed to yield any significant amount of solid picrate.

A saturated solution of urea in methanol gave no precipitate with any distillate, indicating the absence of straight chain compounds.[25]

Twenty ml of the 280° to 290° C fraction were shaken with 20 ml of a saturated solution of thiourea in methanol, and the resultant pasty mass was filtered by suction and the solid washed with cold methanol. Approximately 17 ml of oil were recovered in the filtrate. Decomposition of the crystalline product with water gave 2 to 3 ml of *iso*paraffins and naphthenes, but, since the stability of the thiourea complexes is relatively low,[26] the proportion of these constituents may be appreciably higher than shown by this test.

The crude re-run bottoms frequently possessed a deep red to violet colour, the intensity of which sometimes appeared to be increased on standing or on dilution with methanol; the addition of an acid greatly reduced the colour or changed it to brown, and on distillation this colouring remained in the distillation residue.

Washing the residue with aqueous sodium hydroxide failed to extract the colouring matter, which was, however, readily extracted by alcoholic sodium hydroxide solution, from which it was precipitated on acidification and evaporation of the alcohol (Table XIII).

TABLE XIII

Colouring Matter from Re-run Bottoms

Appearance	Reddish brown pitch
Solubility	Water—insoluble
	Aqueous NaOH—insoluble
	Acetone—readily soluble
	Methanol—readily soluble
	Aromatics—readily soluble
	n-Heptane—sparingly soluble
Colour of methanol solution	Neutral—yellow
	Alkaline—purple violet
pH of colour change	8–9
Sulphur	Present in large amount
Nitrogen	Absent

The fraction in the boiling range of gasoline had an appreciably higher specific gravity and sulphur content (Table XII) than the overhead from the vacuum column of the two-stage distillation of the treated gasoline.

It was, therefore, possible that the residue may have effected an extractive distillation of part of the sulphur compounds present.

A weighed amount of the re-run bottoms was heated with flowers of sulphur to 270° C under reflux, the gases evolved being absorbed in 20 per cent sodium hydroxide solution. Two experiments were carried out, heating for 30 and 120 min at 270° C, at the end of which the oil was converted to a black viscous tar. The unreacted oil was distilled off, washed with sodium hydroxide solution and water, and the specific gravity and sulphur content determined (Table XIV).

TABLE XIV

Action of Elemental Sulphur on Re-run Bottoms

Conditions and results	Experiment No.	
	1	2
Crude re-run bottoms taken, g	100	151
Sulphur added, g	18	27
Temp of action, ° C	270–280	270–280
Time of the action, min	120	30
Loss of wt during reaction, g	17·4	26
Oil recovered as distillate up to 300° C, g	42·5 *	99·5
Oil recovered after alkaline wash, g	34·5	90·0
Sulphur content of washed recovered oil, %	5·28	4·15
Sp. gr. of washed recovered oil	0·940	0·940
Sulphur evolved as hydrogen sulphide, g	7·34 *	20·9
Distillation residue (pitch), g	—	48

* Low recoveries due to a leakage of vapours from the apparatus during refluxing.

Acidification of the sodium hydroxide solution used to wash the distillate oil precipitated a very viscous, heavy brown oil with an obnoxious odour.

Several nitration experiments were made on the 290° to 300° C fraction of the bottoms, in which nitric acid at room temperature was added dropwise to 100 ml of oil and shaken. When approximately 33 per cent by vol of the acid had been added, the acid and oil suddenly reacted very energetically with almost explosive violence, evolving nitrous fumes.

TABLE XV

Products of Nitration of 290° to 300° C Fraction with Concentrated Nitric Acid

Extraction with	Colour of extract	Behaviour with acids	Diazotation and coupled with β-naphthol	Approx quantities	Probable types of constituents
Water	Yellow	No precipitate	—	Traces	Poly-nitrophenols carboxylic acids
Na_2CO_3 + $NaHCO_3$	Orange	Ppt.	Yellow-green dye	Small	Nitro - carboxylic acids; carboxy-acids
NaOH	Brown	,,	(1) Green dye * (2) Yellow dye	Considerable	Nitrophenols
Residue	Dark brown	—	—	Main	Polymers and resins

* Separated by fractional crystallization. Green dye contained nitrogen, no sulphur.

The resultant product, a reddish-brown resin, was successively extracted with water, sodium carbonate–bicarbonate solution, and sodium hydroxide solution. The extracts were acidified and precipitates reduced with tin and hydrochloric acid, diazotized at 0° C, and coupled with alkaline β-naphthol. The results are presented in Table XV.

The re-run bottoms (100 ml) and the acid (124 ml) remained unstirred in two separate layers for 150 to 160 hr at room temperature and gradually turned brown, later reddish-brown, and finally became semi-solid and resinous. The resinous product was extracted with alkalis and examined (Table XVI).

TABLE XVI

Products of Treatment of 290° to 300° C Fraction with Cold 7N-nitric Acid

Extraction with	Diazotation	Qualitative tests for nitrogen–sulphur	Approx quantities	Probable types of constituents
Water	—	—	Traces	Poly-nitrophenols
Na_2CO_3 + $NaHCO_3$	Negative	Negative–positive	Small	Carboxylic acids more soluble
NaOH	Negative	Trace positive	Considerable	Carboxylic acids, less soluble, forming sodium salts
Residue	—	Negative–positive	Main	Polymers and resins

When the bottoms and acid were stirred the colour of the oil changed from the original dark yellow through brown and then green-brown to reddish-brown.

After 20 min stirring the reaction took place with almost explosive violence. The resultant product was cooled, washed, dissolved in butanol, and reduced to 10 hr with tin and zinc in hydrochloric acid, after which the acid aqueous layer showed no presence of aromatic amines. The resinous product contained sulphur and only traces of nitrogen.

One hundred g of the 220° to 320° C fraction were treated with 1 litre of concentrated nitric acid diluted with 500 ml of water and the mixture stirred strongly. Vigorous evolution of nitrous fumes soon set in and, when the reaction subsided, the reddish-brown oil was separated and boiled with 500 ml fresh concentrated nitric acid for 10 min with stirring, large amounts of nitrous fumes being evolved.

After cooling to room temperature an equal volume of cold water was added and the red nitrated product separated and washed with water. It was then boiled with several lots of water until no further acid was removed by the procedure, after which it was dissolved in an excess of methanol and the methanol solution extracted with *n*-heptane. The methanol solution was poured into a large volume of water and the precipitated nitro product filtered off and dried *in vacuo*.

The product was hard and resinous when cold, but softened over a wide temperature range (Table XVII). Attempts to distil it were unsuccessful, as it started to decompose at 140° C. It was soluble in glacial acetic acid, an excess of hot concentrated nitric acid, methanol, ethanol, and higher alcohols, slightly soluble in cold benzene but more soluble in hot benzene, and insoluble in petroleum ether and *n*-heptane. It was also soluble in

dilute caustic soda to a red-brown solution, from which it was quantitatively precipitated by mineral acids but not by acetic acid.

A mixture of 40 ml concentrated nitric acid and 200 ml concentrated hydrochloric acid was added to 10 g of the 220° to 320° C fraction with vigorous stirring and cooling. After 5 min the mixture was heated to boiling under reflux for 15 min, after which it was cooled to room temperature and poured into cold water. The reddish-yellow resin precipitate was washed free from acids with boiling water.

TABLE XVII

Nitro Products from Re-run Bottoms

Product	Dinitro	Chlor nitro
Product yield, % w	80	140
% theory	56	93
Oil recovered, % w	5	Nil
Product sp. gr.	1·0	1·0
Brittle at, ° C	10	20
Soft and ductile at, ° C	30	35
Liquid at, ° C	Approx 50	70
Acid No.	382 *	n.d.
Sulphur content, % w	1·5 †	1·50 †‡
Nitrogen content, % w	9·0 (theor. 9·25)	4·18 (theor. 4·56)
Total chlorine, % w	—	13·0 (theor. 11·6)

* Corresponds to approx 2 mol KOH per mol dinitro compound.

† Identical results obtained by IP 63/51(T) or by refluxing with excess concentrated nitric acid in the presence of barium nitrate until completely oxidized (8 to 10 hr).

‡ This result appears to be somewhat low, probably because of analytical difficulties.

The product was less soluble in methanol and glacial acetic acid than the dinitro compound but more soluble in acetone and hot benzene, and could be obtained as semi-crystalline flakes by crystallization from 9 : 1 benzene–*n*-heptane mixture. The solubility in dilute caustic soda appeared to be less than that of the dinitro compound, but it was completely soluble on heating.

The chlorine was completely removed by boiling with alcoholic potassium hydroxide, or by reduction with zinc dust in glacial acetic acid. Only a trace of aromatic amine was formed during the reduction.

Several sulphonation experiments were carried out in the hope that the reaction products would give some data on the composition of the bottoms.

The oil was stirred with the required amount of sulphuric acid at below 25° C, and after ½ hr the mixture was diluted with 30 g of ice with stirring and external cooling. This procedure gave good separation of the reaction mixture.

It was found that the re-run bottoms could be readily sulphonated even with commercial sulphuric acid, but, to obtain reasonably complete sulphonation without excessive reaction time, a weak oleum was required. On dilution with water the sulphonated product was separated into a green acid layer and a green oil which contained unreacted and polymerized oil plus dissolved sulphonic acids. It was almost insoluble in acid or alkali. Neutralization of the acid layer gave a brown sludge which could be emulsified with a fair degree of stability in the absence of electrolytes and had a pH of about 7. When water-washed, this sludge was slightly soluble

in alcohols and readily soluble in ketones. It tended to emulsify on shaking with water and the presence of calcium salts stabilized cream-like water-in-oil emulsions of re-run bottoms containing approximately 40 per cent water. The sludge was insoluble in dilute alkali, but miscible with dilute acids and soluble in concentrated sulphuric acid. It turned green, evolved sulphur dioxide, and slowly precipitated more of the soluble oil when contacted with any acid, that portion which was soluble in the acid being precipitated as a brown sludge on neutralization of the acid. This recovered sludge showed the same solubility and polymerization characteristics as the original material.

The 260° to 270° C fraction of the bottoms was also sulphonated with almost identical results. In each case the recovered oil was not amenable to further sulphonation.

Since mercurous nitrate has been reported to react quantitatively with dialkyl sulphides [27] its action on the bottoms was examined. To eliminate interference from the colouring matters present, this work was carried out on the 280° to 290° C fraction.

A saturated aqueous solution of mercurous nitrate acidified with 1 per cent by volume of concentrated nitric acid produced a voluminous, greyish-olive sludge when shaken with the oil. The sludge was filtered and washed with *n*-heptane to remove oil and then with water. When dried, the precipitate was a blackish powder. The filtered oil gave no further reaction with the mercurous nitrate reagent. The *n*-heptane washings were distilled to remove the solvent from the oil, which was added to that recovered from the initial filtration. The oil was washed with distilled water, dried, and the yield, specific gravity, and sulphur content determined. The reagent removed 11·6 per cent by weight of the oil to yield a solid equivalent to 38 per cent by weight of the oil. All attempts to decompose this solid component into its precursors failed (Table XVIII).

TABLE XVIII

Treatment of 280° to 290° C Fraction with Mercury Salts

Reagent	Nil	Mercurous nitrate	Mercuric sulphate
Oil unreacted, % w	100	88·4	45·1
Sp. gr. at 60° F	0·929	0·927	0·926
Sulphur content of unreacted oil, % w	5·18	5·55	5·75
Oil polymer, % w	—	—	7·0
% of sulphur removed	—	5·2	50·0
Calculated sulphur content of extracted oil	—	2·32	5·41 ‡
Addition compound, % w	—	38	—
M.W. of extracted oil *	—	232	—
Sulphide content of extracted oil, % w †	—	32	—
Sulphide content of original fraction, % w	—	3·7	—

* Assuming 1 mol reacted with 1 mol of oil to give a simple addition compound.
† Assuming M.W. of sulphur compounds the same as the extracted oil.
‡ Neglecting the sulphur content of the oil polymer.

Since mercuric sulphate in 22 per cent sulphuric acid has been reported to react completely with olefins,[28] some of the 280° to 290° C fraction was

washed with this reagent. This produced a voluminous, intensely orange, slimy precipitate which was filtered, washed with *n*-heptane, then with water, and dried. The orange precipitate turned brown when washed with heptane apparently from the removal of the occluded oil.

Dilution of the reagent with water enabled it to precipitate more of the solid product from the previously washed oil. This dilution was continued until the free sulphuric acid content was approximately 5 per cent. The acid washings were then orange coloured and, on standing for about a week, gave a trace of a voluminous orange precipitate. This may have been partly due to hydrolysis of the mercuric sulphate, which can give a yellow precipitate of the basic sulphate in the presence of less than 12 per cent free sulphuric acid.[28]

The residual oil and the heptane extracts were thoroughly water-washed and the heptane removed by distillation. The oil was then distilled to 340° C to separate the unreacted oil from any polymerization products. This residue was a very viscous greenish brown oil. The properties of the oil distillate are given in Table XVIII.

A weighed amount of the oil (20 to 40 g) was shaken with 100 to 200 ml water, and solid potassium permanganate added in two additions at below 55° C. The first reacted almost instantly, producing no precipitate of manganese dioxide but a deep olive-green coloration of the aqueous layer. With the further addition a thick precipitate of manganese dioxide was formed and the colour of the aqueous layer could still be observed on the inner side of the upper part of the funnel on shaking.

After adding the permanganate, the mixture was acidified either with acetic or phosphoric acid and the manganese dioxide reduced with hydrogen peroxide. The recovered oil was separated, washed thoroughly with distilled water, dried, and examined (Table XIX).

TABLE XIX

Permanganate Oxidation of Re-run Bottoms

Sample	Crude bottoms	260°–270° C fraction	260°–270° C fraction	280°–290° C fraction after $HgSO_4$ treatment
Sp. gr. at 60° F	0·960	0·908	0·906	0·929
Sulphur, % w	4·00 *	4·20	4·20	5·75
$KMnO_4$ oil, by w	2 : 1	1 : 1	2 : 1	2 : 1
Recovered oil, % vol	56	90	65	46·5
Sp. gr. at 60° F	0·981	—	0·942	1·029
Sulphur, % w	3·57	4·67	3·36	4·19
Acid value, mg KOH/g	14·1	—	12·2	—
Reaction with mercurous nitrate	—	†	Nil	—
Alkali soluble oxidn product, % w of oil	—	—	—	1·7
Percentage of sulphur oxidized	50	Nil	48	41·1 ‡

* Neglecting sulphate in ash.
† Converted to greasy grey paste.
‡ Determined as sulphate in the aqueous layers.

The aqueous layer from the oxidation of the 260° to 270° C fraction with 200 per cent by weight of permanganate was found to contain sulphate but no significant amount of carbonate. It gave no precipitate with calcium chloride solution, suggesting the absence of oxalic and other dibasic acids as well as benzoic and related acids. The lower (volatile) fatty acids were found to be present in the distillate from the acidified solution, and the presence of some formic acid was indicated by the reduction of permanganate. Acetic acid was shown to be present by the red colour given with ferric chloride solution, and a trace of butyric acid was indicated by odour.

Identical results were obtained from the examination of the aqueous layer from the oxidation of the crude re-run bottoms.

However, the aqueous layer from this oxidation of the 280° to 290° C fraction after treatment with mercuric sulphate contained a large proportion of carbonate, and on acidification and extraction with ether yielded 1·7 per cent of resin. This was dissolved in dilute sodium hydroxide, and gave a precipitate with barium chloride solution suggesting that it could be a mixture of benzene and thiophene carboxylic acids.

A solution of 5 g of potassium permanganate in 100 ml acetone was added to 10 g of the 220° to 320° C fraction dissolved in 100 ml acetone over a period of ½ hr with strong cooling (max 250° C) and stirring. After 8 hr all the permanganate had been reduced. The solution was filtered from the precipitated manganese dioxide, the acetone distilled off, and the residual oil washed with hot dilute caustic soda solution and redistilled to 320° C. No fatty or naphthenic acids could be detected in the caustic wash, but traces of sulphonic acids were found.

Cracking experiments were carried out on 200 ml of crude bottoms (topped to 200° C) in a 400-ml high pressure gas-heated autoclave equipped with a high range pressure gauge. The charge autoclave was maintained at a temperature of 400° to 420° C for an hour when the pressure reached 1500 to 1600 p.s.i. The autoclave was then quickly cooled and the gases vented through a caustic soda wash bottle. The amount of hydrogen sulphide absorbed was determined by titration with 0·1*N*-iodine. The cracked residue was then distilled to 320° C, washed with dilute caustic soda to remove tar acids, and redistilled into various boiling range fractions (Table XX).

TABLE XX

*Comparison of Crude * and Cracked Re-run Bottoms*

Fraction	% vol †		Sp. gr. at 60° F		Aniline pt, ° C		Br. No. ‡		S % w	
	Crude	Cracked	Crude	Cracked	Crude	Cracked	Crude	Cracked	Crude	Cracked
70°–200° C .	2	22	0·795	0·810	1·0	− 4	6·1	3·9	1·0	6·0
200°–220° C .	4	4	0·850	0·870	1·0	−13	7·4	3·8	1·8	5·1
220°–320° C .	89·5	25	0·870	0·921	1·5	−15	8·5	3·0	4·15	4·2
Residues . .	1·5	20	1·2	1·2	—	—	—	—	4·0	3·5
Cresols + xylenols	3	10	n.d.	1·05	—	—	—	—	—	—
Gas, % . .	Nil	19 §	—	—	—	—	—	—	Nil	7–8 ‖

* Distilled to 320° C.
† Per cent by volume of charge.
‡ By Francis method. This method, although giving low results was adopted for simplicity as it was felt that the results obtained should be comparable.
§ Approximate proportion of charge lost as gas.
‖ Per cent by volume of hydrogen sulphide.

Five g of anhydrous aluminium chloride were added to 20 g of the 220° to 320° C fraction with good stirring, after which the temperature was raised to 90° C and held there for 15 min. On cooling the mixture separated into a layer of brown oil on top of a pitchy solid. The oil was separated, washed with concentrated hydrochloric acid and then with water, and followed by distillation to 320° C.

Ten g of the 220° to 320° C fraction were stirred with 5 g of clean sodium metal and the temperature raised slowly to 200° C. After 15 min the reaction mixture had darkened appreciably. The oil was then separated and distilled up to 320° C.

Dehydrogenation with sulphur was carried out as described previously but without washing the gases evolved. The oil recovered was redistilled to 320° C.

Discussion

The Effect of Treatment Conditions

The contact times of laboratory acid treatments are longer than those of commercial operation, and the increase in secondary reactions (sulphonation and oxidation) results in a greater treatment loss because the reaction products pass into the sludge (Table XXI and Fig 2). With

Table XXI

Effect of Mixing Time

(Using 5 lb H_2SO_4 per brl)

Mixing time, min	Temp, °C	Treatment loss, % vol	Total sulphur after treat, % w	Distillation				Remarks
				F.B.P., °F	% over	Dist loss, % vol	Total sulphur, % w	
3	30	3·5	0·31	348	94·0	0·5	0·27	Temp aver. 30° C
5	30	3·5	0·30	347	94·0	1·0	0·25	
10	30	3·5	0·32	347	94·0	1·0	0·24	
15	30	3·5	0·31	347	93·5	0·5	0·23	5 lb H_2SO_4 per brl
20	30	3·8	0·29	348	93·0	0·5	0·22	
30	30	4·0	0·30	349	93·0	0·5	0·21	
5	−5	2·5	0·30	344	94·8	0·2	0·29	Temp −5° C
10	−5	3·5	0·30	345	94·3	0·4	0·28	
15	−5	3·5	0·29	346	94·2	0·7	0·28	
20	−5	3·5	0·30	346	94·8	0·3	0·26	5 lb H_2SO_4 per brl
30	−5	3·5	0·29	346	94·5	0·2	0·27	
60	−5	3·5	0·29	346	95·0	0·2	0·25	

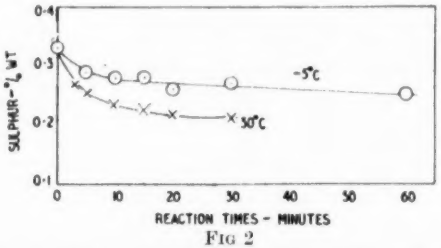


Fig 2

EFFECT OF MIXING TIME ON SULPHUR CONTENT AFTER TREATMENT AND DISTILLATION (USING 5 LB H_2SO_4/BRL)

straight run gasolines, low temperature treatment decreases treatment loss and improves desulphurizing efficiency. For the work described, however, low treatment temperatures resulted in a decrease in efficiency (Fig 3) although reduced treatment losses were obtained. That the polymerizing or alkylating reactions are responsible for the desulphurization of shale gasoline is confirmed by the relationship between treatment loss and decrease in the sulphur content of the distillate treated products (Fig 5).

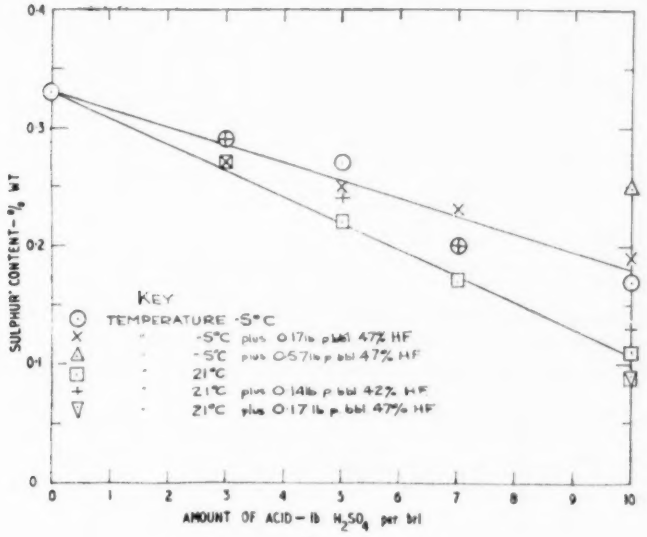

SULPHUR CONTENT – % WT
AMOUNT OF ACID – lb H_2SO_4 per brl
KEY
TEMPERATURE -5°C
-5°C plus 0·17lb p bbl 47% HF
-5°C plus 0·57lb p bbl 47% HF
21°C
21°C plus 0·14lb p bbl 47% HF
21°C plus 0·17 lb p bbl 47% HF

FIG 3

EFFECT OF AMOUNT OF ACID AND ADDITIVES

This infers the formation of high boiling alkyl thiophenes by alkylation of the thiophenes present with the olefins.[9]

As regards acid concentration (Table XXII and Fig 4) 60 per cent acid

TABLE XXII

Effect of Acid Concentration

(10 lb of 98% H_2SO_4 used per brl at 21° C)

Acid strength, % H_2SO_4 w	Treat loss % vol	Total sulphur after treat, % w	Distillation			Total sulphur, % w
			F.B.P. °F	% over	Dist loss, % vol	
Nil	Nil	0·33	341	95·0	0·2	0·32
10	1·5	0·32	341	94·0	1·1	0·31
70	1·0	0·32	342	94·0	1·1	0·28
75	2·0	0·31	344	94·0	1·1	0·26
80	2·5	0·31	343	93·8	0·7	0·23
85	2·7	0·30	344	93·8	0·9	0·22
90	4·0	0·28	342	94·0	0·5	0·18
95	4·0	0·28	343	93·5	0·8	0·13
98	5·5	0·27	342	94·0	0·7	0·11

had practically no desulphurizing action.[5] Desulphurizing efficiency was related to treatment loss (Fig 5).

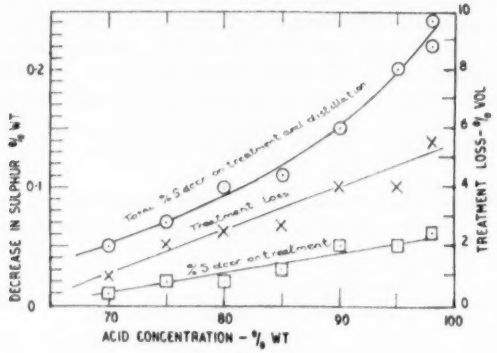


FIG 4

EFFECT OF ACID CONCENTRATION

Hydrofluoric acid exhibits catalytic properties in alkylation reactions, but its effect with shale gasoline was found to be negligible, even after allowing for the dilution of the sulphuric acid (Table XXIII and Fig 3).

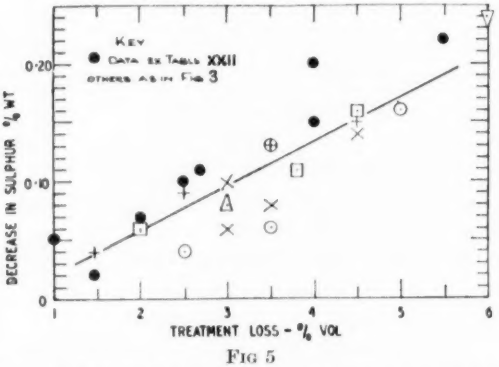


FIG 5

RELATIONSHIP BETWEEN TREATMENT LOSS AND DESULPHURIZATION

The effect of using copper sulphate as a treatment catalyst in sulphuric acid [8] was negligible, and it would therefore appear that the condensation of thiophenes with aldehydes [6] and ketones [7] during acid treatment does not take place to any significant extent.

Effect on Octane Rating and Lead Susceptibility of Shale Naphtha (Figs 6 and 7)

The sulphur content was decreased (Fig 8) appreciably to an extent which indicated chemical as well as physical removal of sulphur com-

TABLE XXIII

Effect of Amount of Acid

98% H_2SO_4 lb per brl	Effective H_2SO_4 concn	Temp °C	HF added lb per brl	Treat loss	Total sulphur after treat, % w	F.B.P., °F	Distillation		
							% over	Dist, % vol	Total sulphur % w
3	98	−5	Nil	2·5	0·31	346	94·8	0·3	0·29
5	98	−5	Nil	3·5	0·29	346	94·5	0·2	0·27
7	98	−5	Nil	3·5	0·28	345	94·0	0·6	0·20
10	98	−5	Nil	5·0	0·26	345	94·2	0·6	0·17
3	95·3	−5	0·17 *	3·0	0·30	345	94·5	0·5	0·27
5	96·5	−5	0·17 *	3·5	0·30	345	94·6	0·5	0·25
7	96·8	−5	0·17 *	3·0	0·30	344	94·0	0·7	0·23
10	97·3	−5	0·17 *	4·5	0·29	344	94·0	0·7	0·19
10	95·2	−5	0·57 *	3·0	0·33	346	94·5	0·6	0·25
3	98	21	Nil	2·0	0·30	346	94·8	Nil	0·27
5	98	21	Nil	3·8	0·27	346	93·5	0·6	0·22
7	98	21	Nil	4·5	0·28	345	94·0	0·4	0·17
10	98	21	Nil	8·0	0·28	346	93·0	1·2	0·09
10	97·3	21	0·17 *	6·0	0·24	345	93·6	0·4	0·09
3	95·4	21	0·14 †	1·5	0·32	342	94·5	0·6	0·29
5	96·5	21	0·14 †	2·5	0·31	344	94·2	0·8	0·24
7	96·8	21	0·14 †	3·5	0·31	344	94·1	0·8	0·20
10	97·2	21	0·14 †	4·5	0·29	343	94·0	0·5	0·13

* 47% HF †42% HF

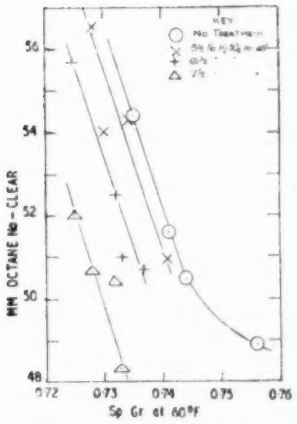


FIG 6

RELATIONSHIP BETWEEN 80% POINT AND CLEAR O.N.

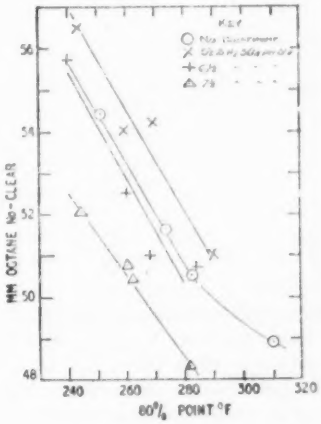


FIG 7

RELATIONSHIP BETWEEN SP. GR. AND CLEAR O.N.

O

pounds (largely thiophenic). This also could be explained by the alkylation of the thiophenes by the olefins present.[9]

As regards the effect of treatment on lead response, shown graphically in Fig 9, it is to be observed that high boiling point exerted no influence.

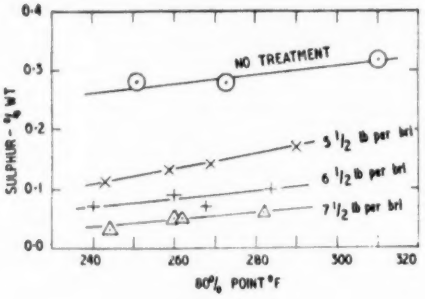


FIG 8

EFFECT OF TREATMENT ON SULPHUR CONTENT

The octane rating of the unleaded gasoline first increased and then decreased with increase in acid treatment, the maximum octane number being obtained with a treatment of between 3 and 4 lb acid per barrel. A subsequent stock of naphtha with a lower end point failed to provide the same relationship between clear octane number and degree of treatment, although the desulphurizing effect was much greater. From this it would appear that the sulphur compounds are more readily removed than some

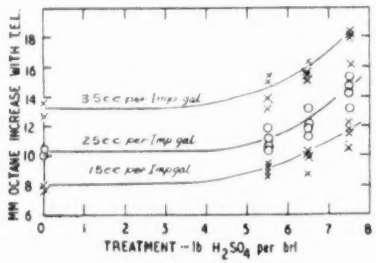


FIG 9

EFFECT OF TREATMENT ON TEL RESPONSE

of the higher octane number constituents, which deduction is in agreement with the removal of the alkyl thiophenes with the residue from the redistillation step.

Further increases in acid treatment caused decreases in octane number, due presumably to the removal of some of the high octane number aromatics and olefins by sulphonation and polymerization. In Fig 10 it will be appreciated that the slightly greater TEL responses could be due to the lower sulphur content. Thus, considerations of octane rating and lead

susceptibility provide further indirect support for the thiophene alkylation explanation of the high desulphurization efficiency.

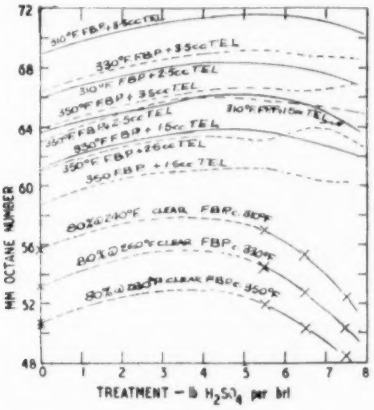


FIG 10

EFFECT OF TREATMENT ON O.N.

Removal of Thiophenes

The work with benzole indicated that the reaction resulted in thiophene removal and that ammonia could be replaced by other amines, including pyridine homologues. In the presence of oxidation products, such as aldehydes, the tar bases in cracked shale gasoline can react selectively with the thiophenes during acid treatment to give acid-soluble products and possibly also dithienylalkyl methanes which would be removed in the redistillation residue. This is in agreement with plant observations that oxidized gasoline responds more readily to acid treatment.

Since 2-alkyl thiophenes react as readily as thiophene,[13] the small decrease in sulphur content indicates that the bulk of the thiophenes present were substituted in both the 2 and the 5 positions. Consequently the increased desulphurization is not sufficient to warrant any more than a minor modification of the acid treatment process with this gasoline.

Neutralization

One-fifth of the acidity of the gasoline after separation from acid tar is due to organic acids which could be determined by titration to methyl orange end point. They are probably alkyl sulphuric acids and aryl sulphonic acids. As the raw gasoline contains only 8 per cent of aromatics against 50 per cent of olefins the proportion of aryl sulphonic acids formed would be less than that of the alkyl sulphuric acids.

The greatly increased rate of hydrolysis of the solution after acidification [20] confirms the suggestion that the products are principally alkyl sulphuric acids. The presence of alcohols in the oil obtained from the spent solution by distillation was confirmed, and ketones have been isolated from acid sludge by other workers,[21, 22] and it seems probable that they will form by oxidation in the sludge of secondary alcohols or alkyl sulphonates. The

presence of methyl-ethyl-ketone in the oil from the neutralization caustic wash suggests that either the ketone was initially present or that it was formed from traces of butene remaining in the topped gasoline. An alternative but less probable mechanism would involve the destructive oxidation of 2-alkyl-2-alkene.

By evaporation and destructive distillation of 400 gal (24,000 gal of gasoline treated per day) of spent caustic soda solution, 48 gal of heavy yellow oil may be obtained; this is obviously derived from the alkyl sulphates, of which the bulk was removed from the gasoline by the water wash and only 20 per cent by the caustic wash. Therefore, approximately 240 gal of this oil are lost from the 24,000 gal of gasoline treated (*i.e.*, 1 per cent) and since the olefin content of the gasoline was approximately 50 per cent, the alkyl sulphates are formed to the extent of about 2 per cent of the olefins present.

Examination of Re-run Bottoms

The average molecular weight of the distillation bottoms is approximately twice that of the gasoline, indicating the condensation of an average of two probably dissimilar molecules of the gasoline. The 7 per cent

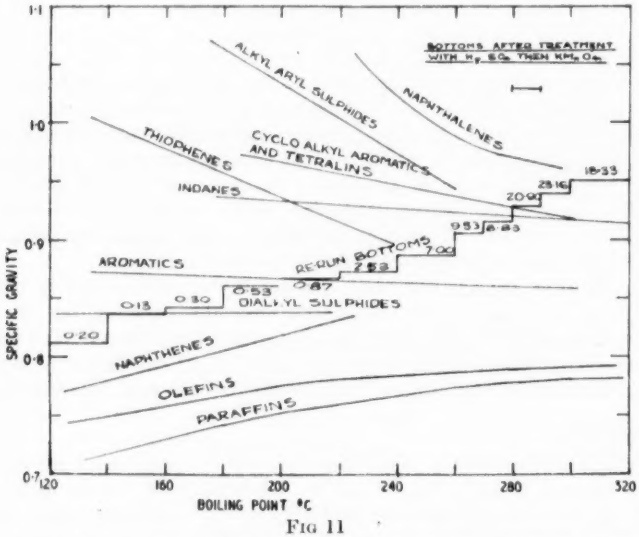


FIG 11

BOILING POINT–SP. GR. RELATIONSHIPS OF RE-RUN BOTTOMS. FIGURES DENOTE PER CENT VOL OF THE VARIOUS FRACTIONS (THEORETICAL DATA FROM REFS 30, 31)

residue from the steam distillation is an indication of the extent of polymerization, including a disproportionation and polymerization of the olefin dimers, although a considerable proportion of tars as well as neutral oils are present in the acid sludge.[29] As the boiling points of the fractions increase, the specific gravities increase, varying between those of aromatic and other hydrocarbons to those approaching alkyl naphthalenes (Fig 11).

This would appear to suggest the presence of polycyclic aromatics, particularly in the high boiling fractions of the residue. The failure to precipitate any hydrocarbon picrates does not over-rule this possibility, which is further supported by the solubility characteristics of the residue from steam distillation.

Treatment with urea indicated that straight chain compounds were absent, while thiourea indicated the presence of about 15 per cent of *iso*-paraffins and naphthenes probably accompanied by corresponding olefins.[32,33]

The organic sulphur present in crude residue (Table XII) (mol. wt. 195) corresponds to 24 per cent by weight of sulphur compounds (alkylated thiophenes) with one sulphur atom per molecule.

The absence of mercaptans and disulphides indicates that those mercaptans removed by treatment had not been oxidized but had reacted in some other manner, probably by alkylation, to give dialkyl sulphides which were found to be present by treatment with mercurous nitrate but absence of di- and polysulphides was confirmed by the relative stability of the oils to the copper strip test.

It is probable that the phenols present in the higher fractions include some which were alkylated [29] with the lower boiling olefins together with some phenols liberated from the alkylated products by mild cracking during distillation. The comparatively high phenol content of the 300° to 320° C fraction supports this suggestion. The colours obtained by treatment with hydrochloric acid may be due to some acid unstable compounds such as pyrroles, which are known to be present in the gasoline.[34-37] Some of these may have been alkylated and thus appear in the residue.

The colouring matter present is obviously of high molecular weight, and probably contains an acidic group in the molecules as shown by the colour change in the presence of alkalis. This may be a phenolic hydroxide or a sulphonic acid, the large amount of sulphur being present in a paraffin ring or in a sulphonic acid group.

Heating the distillation bottoms with elemental sulphur resulted mainly in dehydrogenation with the formation of tars, little if any of the sulphur entering into the structure of the oil. This is in agreement with the presence of naphthene rings in the bottoms being dehydrogenated with the formation of tars, the aromatics and thiophenes being only partially attacked.

Sulphonation gave both oil- and water-soluble sulphonic acids, thus indicating that both long chain and short chain alkyl aromatics were present.[38-41] Sulphuric acid also exerts an oxidizing and condensing action which converts a proportion to neutral resins and asphaltenes which are subsequently sulphonated.

Treatment of the 280° to 290° C fraction with mercurous nitrate removed 11·6 per cent by weight of the oil, of which only 3·7 per cent could be sulphur compounds. These would be dialkyl sulphides [42] and would have been formed by the condensing of olefins with mercaptans during acid treatment.

In addition to the olefins, acid mercuric sulphate solution removes half the sulphur compounds present,[43] but if it is assumed that the sulphur compounds removed were thiophenes, then they together with any olefins

TABLE XXIV

Reactions that can take place during the acid treatment of gasoline * to give rise to the formation of "re-run bottoms"					Results			
Reaction No.	Constituent	Reactant	Reaction type	Product	Identification of product	Approx proportion	Reagent or method	Remarks
1	Olefins	Paraffin or naphthenes	Alkylation	Higher M.W. paraffins or naphthenes	Yes	10–15% 5%	Thiourea Nitration residue	*n*-paraffins absent
2	Olefins	Aromatics	Alkylation	Alkyl aromatics	Yes	Present	Nitration and sulphonation	—
3	Olefins	Olefins	Polymerization	Olefin polymer	Yes	10%	Bromine No.	—
4	Olefins	Conjugated diolefins	Co-polymerization	Olefin polymer			Permanganate oxidn	
5	1-Alkenes	Aldehydes in presence of acyl peroxides	Condensation	Ketones	n.d.	—	—	—
6	Olefins	Mercaptans	Alkylation	Dialkyl sulphide	Yes	3·7% in 280–290° C fraction	Mercurous nitrate	Cf. Nos 15 and 16
7	Olefins	Thiophenes	Alkylation	Alkyl thiophenes	Yes	—	High sp. gr. and % S and cracking	—
8	Olefins	Thiophenes	Condensation	"Coloured products"	?	—	—	Colouring matters present
9	Olefins	Phenols	Alkylation	Alkyl phenols	Yes	10%	Cracking	—
10	Olefins	Phenols	Condensation	Coloured condensation products	?	—	—	Colouring matters present
11	Olefins	Sulphuric acid	Disproportionation	Paraffins and diolefins, tars, etc.	Yes	8% tar	Distillation residue	—
12	Naphthenes	Phenols	Condensation	"Condensation products"	?	—	—	Tars present
13	Mercaptans	Sulphuric acid	Esterification	Alkyl thiosulphates and dialkyl thiosulphates	—	—	—	—
			Esterification and decomposition	Dialkyl disulphide	Absent	Nil	Reduction to mercaptans	—
			Oxidation (overall)	Dialkyl disulphide				
14	Mercaptans	Sulphuric acid and sulphur	Oxidation	Dialkyl trisulphide	Absent	Nil	Copper strip test	—
15	Mercaptans	Alkyl sulphate (from olefin)	Alkylation	Dialkyl sulphides	Yes	3·7% in 280°–290° C	Mercurous nitrate	Cf. Nos 6 and 16
16	Mercaptans	Aryl sulphonic acids	Condensation	Alkyl aryl sulphides	?	—	—	Would be included with dialkylsulphides Nos. 6 and 15
17	Mercaptans	Aldehydes	Condensation	Mercaptals	Absent	Nil	Would respond to tests for mercaptans which were absent	—
18	Mercaptans	Ketones	Condensation	Mercaptoles		Nil		
19	Alkyl sulphides	Sulphuric acid	Oxidation	Sulphones	N.d.	—	—	—
20	Thiophenes	Sulphuric acid	Polymerization	Coloured materials, resins, and polymers	Probable	—	High sp. gr. and % S and cracking	Colouring matters present
21	Thiophenes	Aldehydes	Condensation	Resins	—	—	—	Tars present
22	Thiophenes	Aldehydes in presence of nitrogen salts	Aminomethylation then condensation	Dithienylmethanes	Possible	—	High sp. gr. and % S and cracking	—

* This part of the table is abridged from a more complete table of reactions that can take place during the acid treatment of gasoline.[4]

would account for about half of the large proportion of oil removed by the reagent.

Treatment with neutral permanganate brought about the oxidation of about half of the sulphur compounds. Volatile fatty acids were formed, indicating the presence of side chains. The results suggest a successive oxidation of the various classes of constituents of the residue, beginning with the olefins and the more reactive side chains, followed by some of the sulphur compounds and less reactive hydrocarbons. Oxidation of *cyclo*-alkene or naphthene rings, particularly if fused to another ring, would explain the increase in the already high specific gravity.

In addition to the information in Table XXIV, the following reactions are suggested :—

(1) cyclization of alkyl aromatics to yield alkyl tetralins or indanes;
(2) oxidation of *cyclo*alkyl aromatics to give cyclic aromatics;
(3) indole formation from pyrroles by polymerization and decomposition;
(4) alkylation of pyrroles by olefins.

Of these, the first two appear to be probable and the last two possible.

Exhaustive treatment with concentrated sulphuric acid followed by nitric acid gave a 6 per cent yield of saturated residue of a water white oil (Table XXV) consisting of *iso*paraffins and alkylated naphthenes formed

TABLE XXV

Exhaustive Treatment of Re-run Bottoms with Sulphuric Acid

Treatment (successive)	Oil recovered, ml	Sp. gr. at 60° F	S, % w	Aniline pt, ° C	Br. No.
Nil	100	0·925	—	—	—
100 ml H_2SO_4 . .	25·4	0·895	—	—	—
25·4 ml H_2SO_4 . .	15·5	0·868	—	—	4·0
15·5 ml H_2SO_4 . .	11·0	0·868	3·9	36	4·0
40 ml conc HNO_3 (cold).	6·0	0·810	0·5	66	0·0

by the alkylation of paraffins and naphthenes with olefins and also by the disproportionation of olefin polymers formed during acid treatment process. The difference in bromine numbers (McIlnney [3] 40 per cent of olefins, Francis 11 per cent of olefins) may possibly be equivalent to the mean of sulphur compounds present. The aromaticity of the product obtained by cracking the 200° to 220° C fraction (Table XX) suggests the splitting off of side chains of alkyl aromatics and alkyl thiophenes already suggested as being present in the residue. This is supported by the increase in the sulphur content of the gasoline fraction (1 to 6 per cent), which is greater than can be explained satisfactorily by a different mechanism. Further support for this suggestion is the negligible indophenine test for thiophenes before cracking and a positive test after cracking. Furthermore, the large increase in caustic-extractable tar acids on cracking suggests the presence of a large proportion of phenols with long side chains or naphthenyl phenols.

Treatment with anhydrous aluminium chloride, metallic sodium, elemental sulphur, or permanganate in acetone solution gave little information

regarding composition of the residue (Table XXVI), and similar extractions with methanol failed to afford any concentration of the sulphur compounds,

TABLE XXVI

Miscellaneous Treatments of Re-run Bottoms

Treatment	Oil recovered, % w	Sp. gr. at 60° F	S, % w	Aniline, pt, ° C	Br. No.
Nil	100	0·870	4·15	1·5	8·5
25% w $AlCl_3$	45	0·875	3·2	29·5	—
50% w Na metal	60	0·858	4·0	20·5	—
10% w sulphur	30	0·970	5·0	—	8
50% w $KMnO_4$ in acetone	80	0·860	3·4	2	—

although crystallization from acetone [45] at −60° C gave a relatively low sulphur fraction (Table XXVII).

TABLE XXVII

Solvent Extraction of Re-run Bottoms

Fraction	Solvent	Extraction temp, ° C	Vol, %	Sp. gr. at 60° F	Aniline pt, ° C	S, % w
Original 220°–320° C	Nil	—	100	0·870	1·5	4·15
Extract	Methanol	Room	20	0·900	−15	5·5
Raffinate	Methanol	Room	80	0·855	5	4·0
Extract	Acetone	−60	63	0·880	−14	5·2
Raffinate (solid)	Acetone	−60	35	0·840	38	2·5

Nitration of the 220° to 320° C fraction with cold concentrated or hot diluted nitric acid gave the same results.

Treatment of the same fraction with an excess of aqua regia gave a high yield of the product which approximated to that of monochlor mononitro derivative (Table XVII). The high yield, however, did not assist in clarifying the composition of the original residue.

It is a further indication of the difficulties underlying examination of the re-run bottoms that this complex mixture of hydrocarbons and sulphur compounds should react so uniformly with nitric acid or aqua regia to give such high yields of the apparently relative uniform structure of the dinitro and chloro nitro derivatives.

In concluding this section it should be pointed out that the re-run bottoms includes only about half of the high boiling by-products of the acid treatment, the other half being dissolved in and separated with the acid sludge.[44] The results obtained therefore cannot be expected to give anything more than a partial picture of the acid treatment process.

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THE INSTITUTE OF PETROLEUM

SPECIAL GENERAL MEETING

A SPECIAL GENERAL MEETING of the Institute of Petroleum was held at 26 Portland Place, London, W.1, on 10 December 1952, to consider and, if thought fit, to pass a resolution to substitute a new By-Law No. 28, to become effective as from 1 January 1953, for the existing By-Law No. 28.

THE PRESIDENT (H. S. Gibson, C.B.E.) occupied the Chair.

THE GENERAL SECRETARY (D. A. Hough) read the notice convening the meeting.

V. BISKE, explaining the reason for this change in the By-Laws, said it concerned office procedure in connexion with the applications for membership of the Institute and transfer from one grade to another. The Institute had a fairly strict Election Committee, and cases occurred where applications were not accepted. The present By-Law stated that no notice should be given to such candidates, and it was proposed to amend this to permit a candidate to receive formal notice of the result of his application.

THE GENERAL SECRETARY read the first part of the resolution, as follows :—

1. That By-Law No. 28, as amended and set out below is hereby approved and adopted as part of the By-Laws of the Institute of Petroleum in substitution for and to the exclusion of the existing By-Law No. 28.

> " In the case of non-election or non-transference no mention shall be made thereof at an Ordinary or General Meeting nor shall the fact be published by the Institute, but the General Secretary shall send to the Candidate a printed form stating only that his application has been unsuccessful."

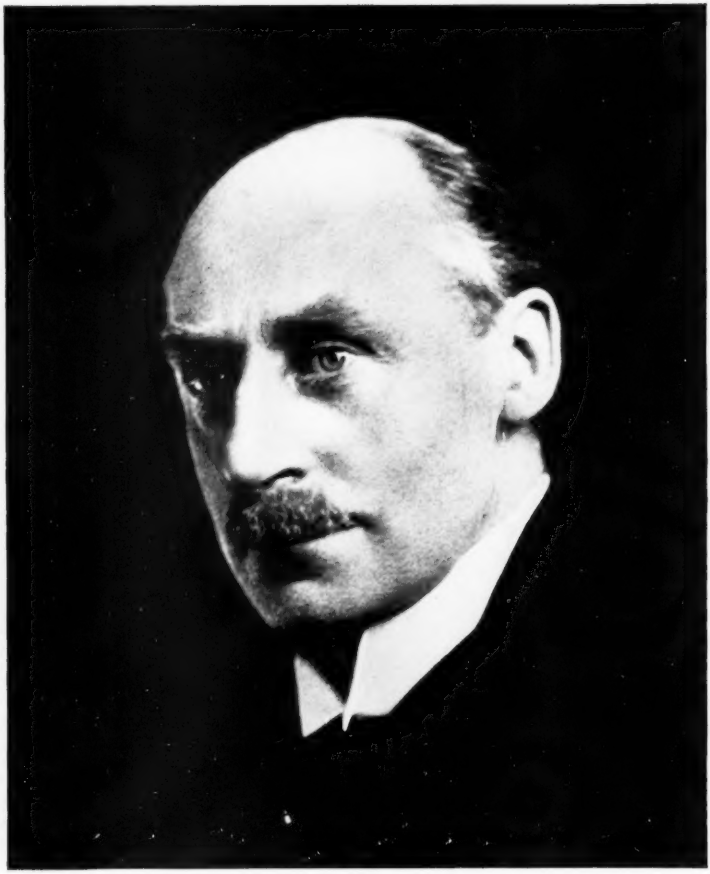
Part 1 of the resolution was proposed by V. Biske, seconded by C. D. Brewer, and carried unaminously.

THE GENERAL SECRETARY read the second part of the resolution :—

2. That By-Law 28, as amended, shall become effective as from 1 January 1953.

Part 2 of the resolution was proposed by V. Biske and seconded by C. D. Brewer, and was carried.

(The business of the Special General Meeting concluded.)



PROFESSOR JOHN SAMUEL STAFFORD BRAME, C.B.E.

1871—1952

President of the Institution of Petroleum Technologists 1921–23

[*To face p.* 183.

OBITUARY

PROFESSOR JOHN SAMUEL STAFFORD BRAME, C.B.E.

WITH the passing of John Samuel Stafford Brame on 10 December 1952 in his eighty-second year, the Institute loses a distinguished member of that rapidly diminishing band of pioneers who laid so well and truly the foundations of the society first known as the Institution of Petroleum Technologists.

His was the generation of Boverton Redwood, Arthur W. Eastlake, Vivian B. Lewes, Thomas Holland, Charles Greenway, and John Cadman, all of whom rose to eminence in the service of petroleum science and in the industry. Brame was elected a Member in 1916, Fellow in 1939, and Hon. Fellow in 1951. He served on Council continuously from 1917 to his death, although in recent years failing health prevented his attendance at meetings. He was president in 1921–23. Perhaps his greatest work for the Institute lay in the direction of standardization. He was chairman of the Standardization Committee from 1929 to 1938 and saw it grow in importance year by year, culminating in the friendly co-operation with the ASTM. He contributed many articles to the technical press, and wrote a well-known and admirable text-book on fuel.

He was connected with the Royal Naval College so far back as 1897 when he joined the staff, being promoted to the Chair of Chemistry in 1914—from this he resigned in 1932. In the New Year Honours List in 1930 he was awarded the C.B.E.

He presided with Major Crozier at a Ministry of Transport inquiry into proposals to allow tankers containing motor spirit to pass higher up the River Thames than had been permitted. In his later years he was on the Board of Alexander Duckham & Co. Ltd., and for many years he conducted evening classes in Petroleum Technology at the Sir John Cass Institute.

In all, he had an active and vigorous outlook on life. He was invariably cheery and optimistic, a delightful companion, and the best of friends.

In all his endeavours he was ably supported and encouraged by Mrs Brame, who survived him by only two days.

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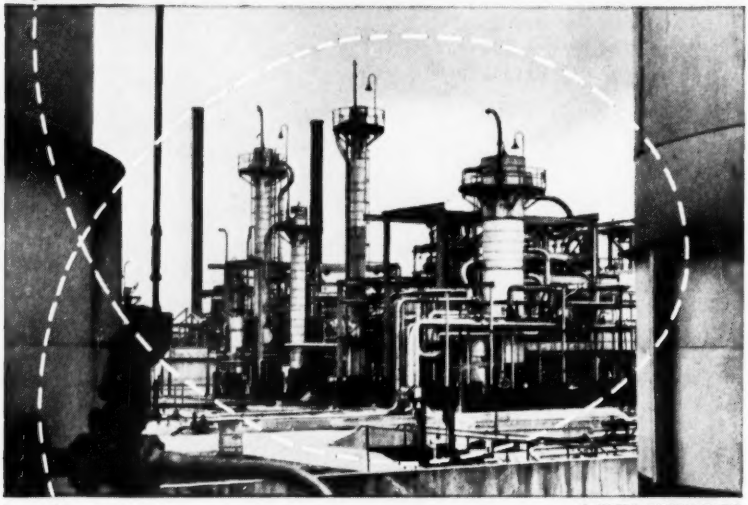

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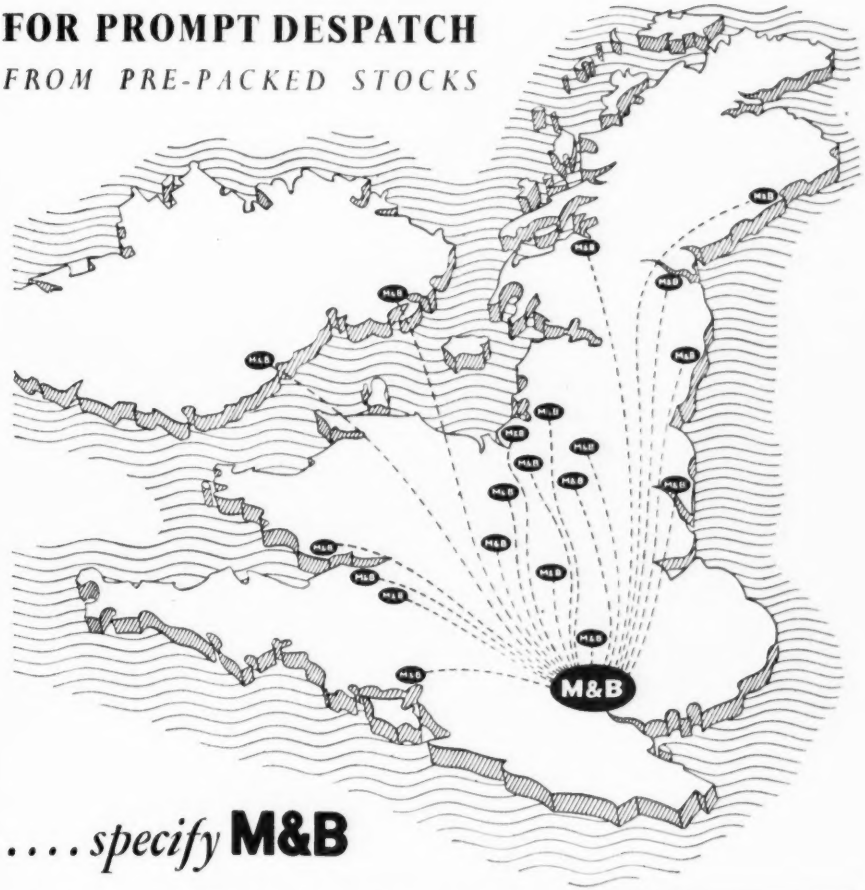

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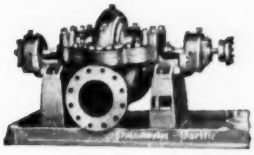

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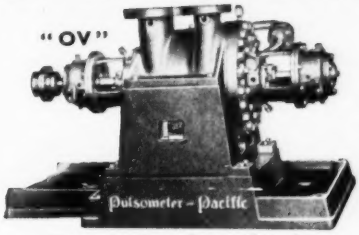

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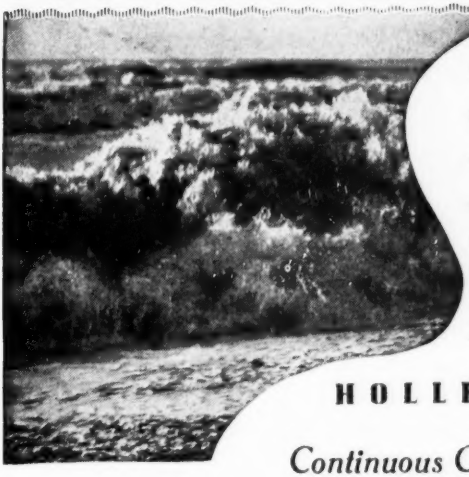

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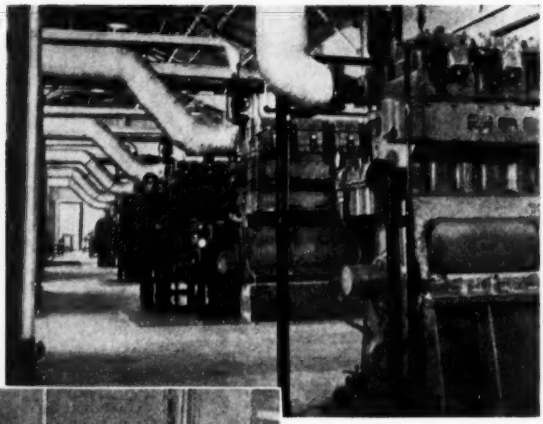

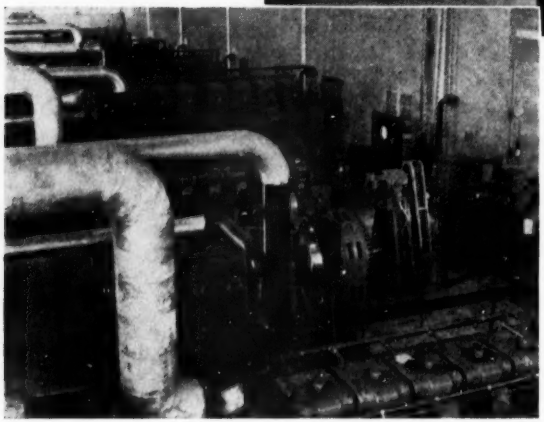

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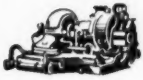

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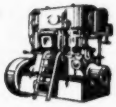

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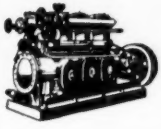

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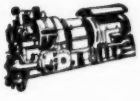

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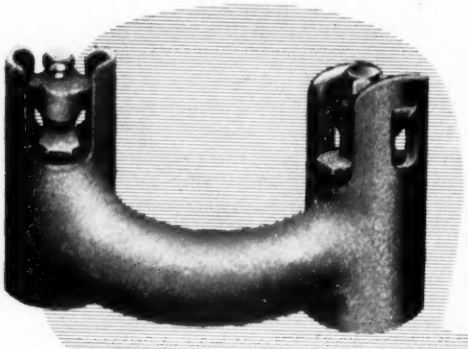

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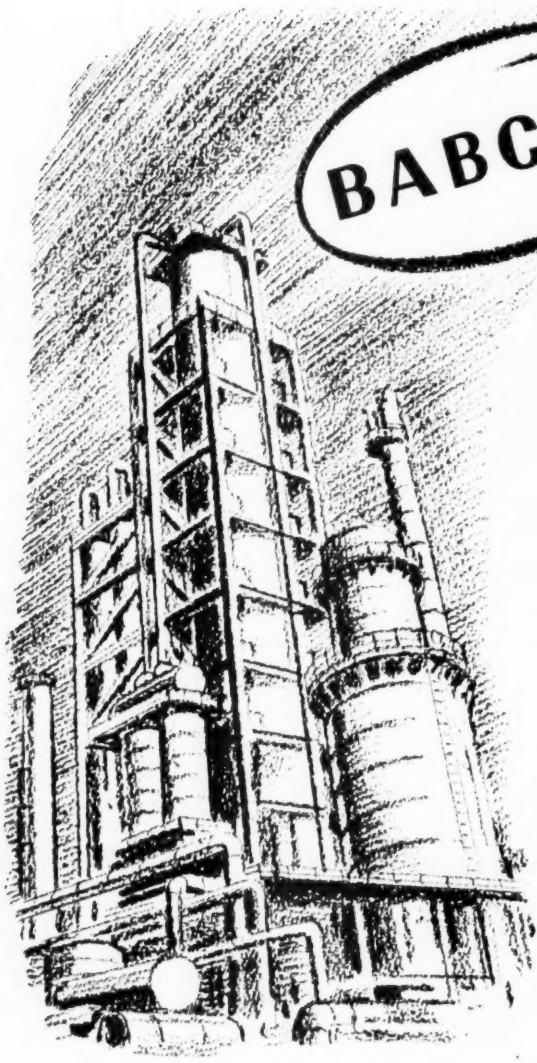

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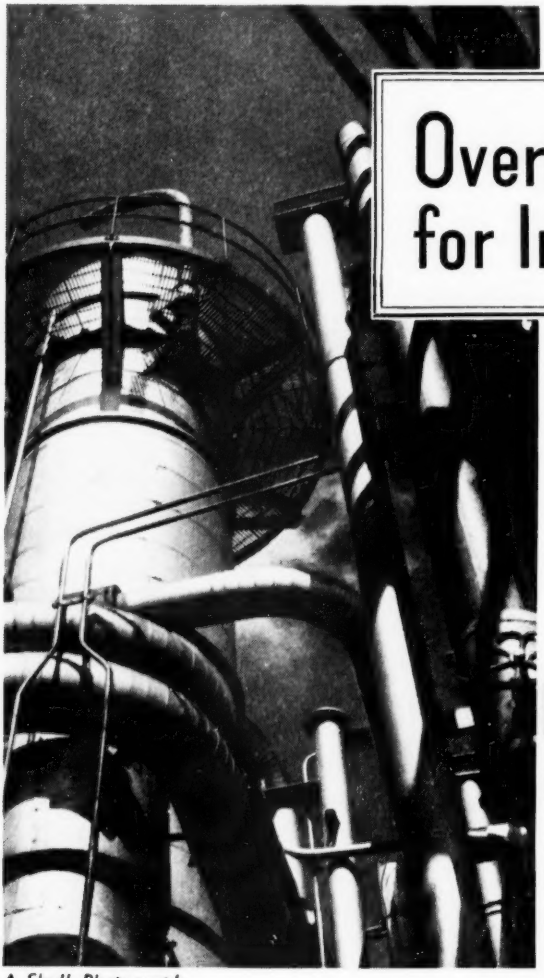

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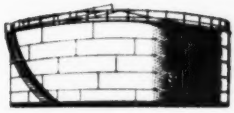

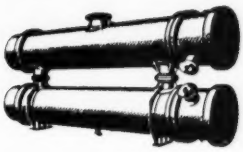

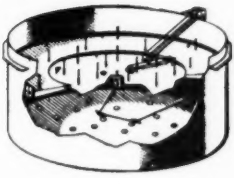

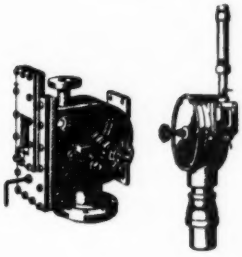

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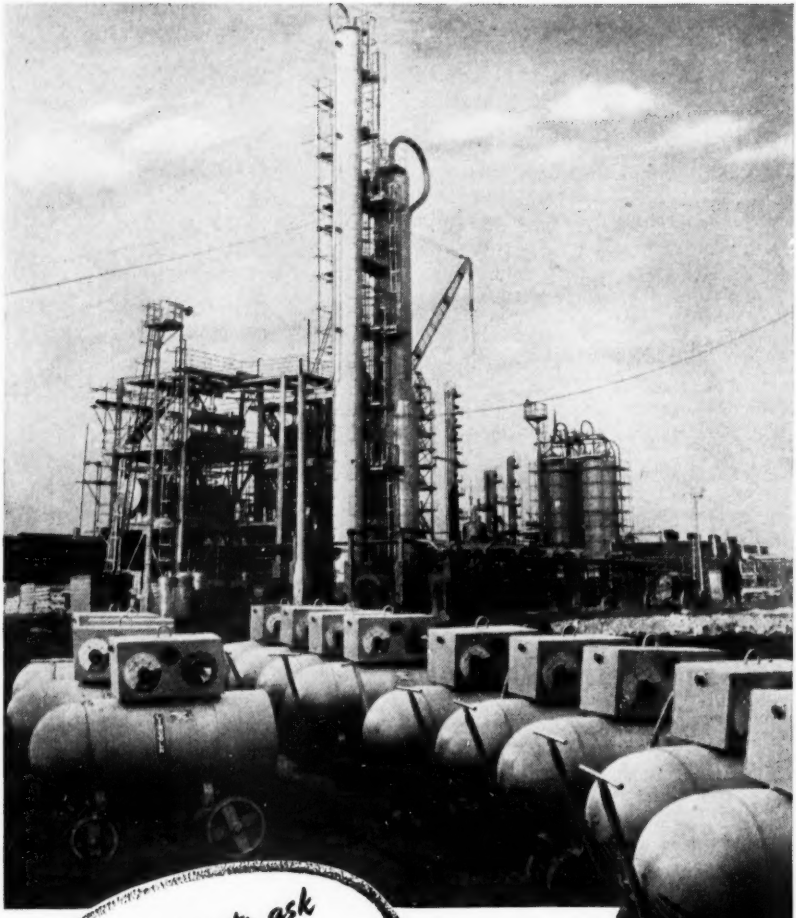

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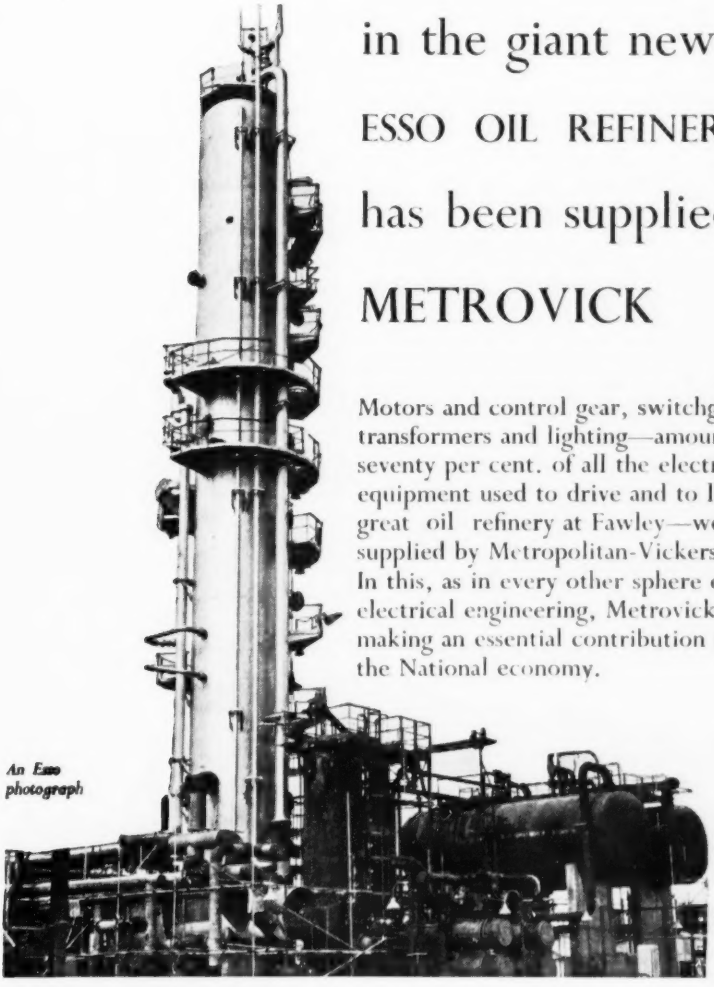

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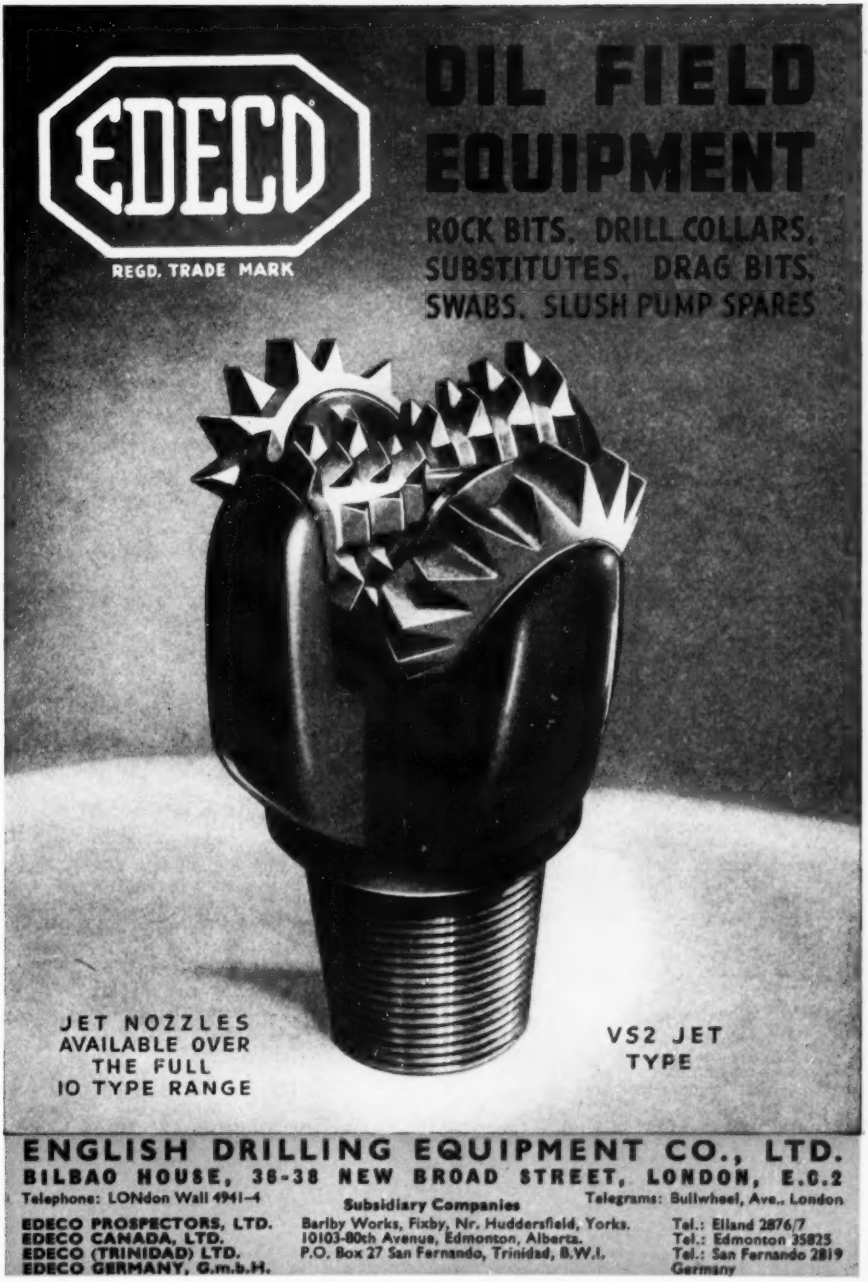
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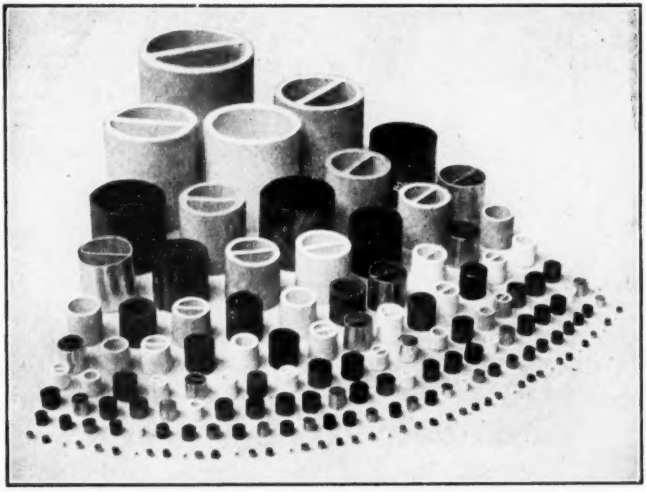

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LIST OF ADVERTISERS

	PAGE
Babcock & Wilcox, Ltd.	x
E. B. Badger & Sons Ltd.	iv
Baird & Tatlock (London) Ltd.	Feb.
Baker Oil Tools, Inc.	Feb.
Birmingham Battery & Metal Co. Ltd. ...	Feb.
British Oilfields Equipment Co. Ltd. ...	Feb.
Peter Brotherhood Ltd.	vii
W. P. Butterfield, Ltd.	xxiii
W. H. Capper & Co. Ltd.	—
Consolidated Pneumatic Tool Co. Ltd.	Feb.
A. F. Craig & Co. Ltd.	i
Crosby Valve & Engineering Co. Ltd. ...	Feb.
Cyanamid Products Ltd.	—
Dorman & Smith Ltd.	Feb.
English Drilling Equipment Co. Ltd. ...	xix
Exactor Ltd.	Jan.
Foxboro-Yoxall, Ltd.	Feb.
W. J. Fraser & Co. Ltd.	ii
Matthew Hall & Co. Ltd.	vi
Hayward Tyler & Co. Ltd.	xxiv
H.M. Continuous Plant Ltd.	v
Hydronyl Syndicate, Ltd.	xx
Wm. Kenyon & Sons, Ltd.	xii
Richard Klinger, Ltd.	xi

	PAGE
Lake & Elliott, Ltd.	xxi
Lincoln Electric Co. Ltd.	xvi
A. & J. Main & Co. Ltd.	xiv
May & Baker Ltd. (Lab. Chemicals) ...	iii
Metal Propellers, Ltd.	xxii
Metropolitan-Vickers Electrical Co. Ltd.	xvii
A. P. Newall & Co. Ltd. ...	Inside Back Cover
Newman, Hender & Co. Ltd.	ix
Newton, Chambers & Co. Ltd.	Feb.
Nicerol, Ltd.	Feb.
Oil Well Supply Co.	Back Cover
Samuel Osborn & Co. Ltd.	viii
Oxford University Press	Feb.
Pulsometer Engineering Co. Ltd. ...	v
Pyrene Co. Ltd.	xiii
Quasi-Arc Co. Ltd.	Feb.
Sigmund Pumps Ltd.	Feb.
Tylors of London, Ltd.	Feb.
Wheesoe, Ltd.	xv
Henry Wiggin & Co. Ltd.	xviii
John Wilkes, Sons & Mapplebeck Ltd. ...	—
W. Martin Winn, Ltd.	xi
Yorkshire Copper Works, Ltd.	Feb.

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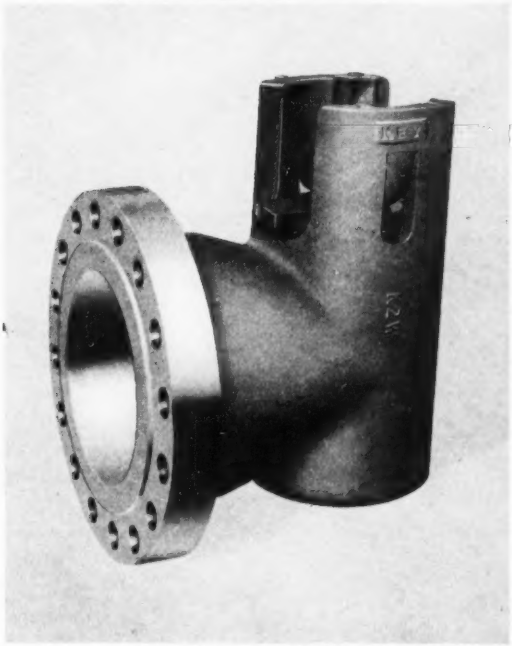

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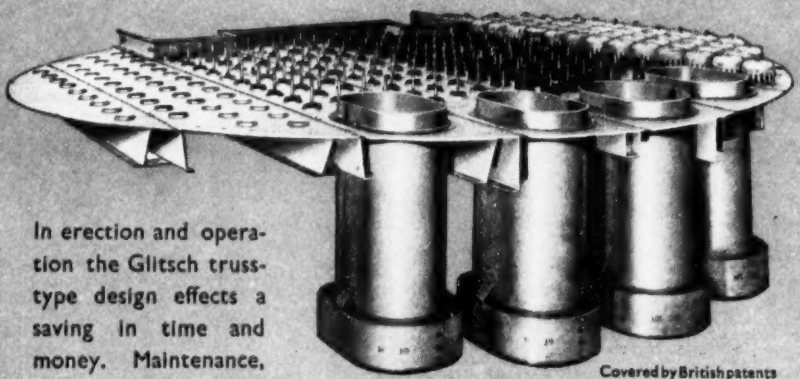

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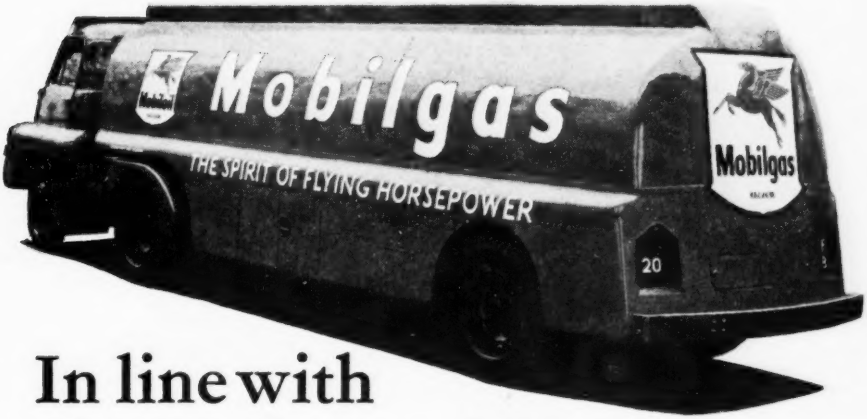

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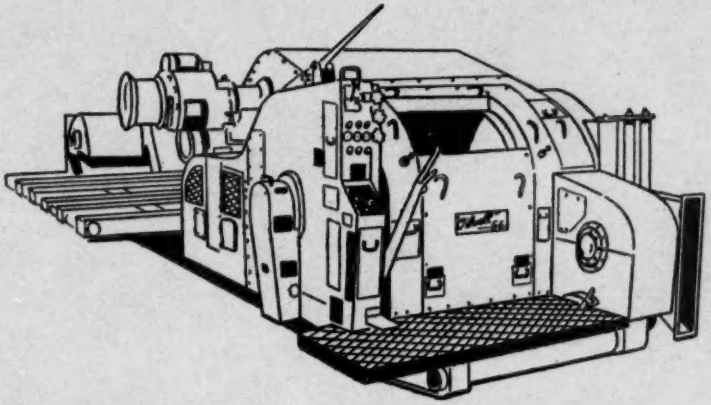

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